Supplementary Information

For

Asymmetric Construction of Allylic Stereogenic Carbon Center Featuring a Trifluoromethyl Group via Enantioselective Reductive Fluoroalkylation

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I. Supplementary Notes

General Information

NMR spectra were recorded on Bruker-500 (500 MHz for \(^1\)H; 126 MHz for \(^{13}\)C and 471 MHz for \(^{19}\)F). All \(^1\)H NMR, \(^{13}\)C NMR and \(^{19}\)F NMR spectra were recorded at room temperature. \(^1\)H NMR spectra were referenced relative to CDCl\(_3\) at \(\delta 7.26\) ppm. \(^{13}\)C NMR spectra were referenced relative to CDCl\(_3\) at \(\delta 77.16\) ppm. The \(^{13}\)C NMR spectra were obtained with \(^1\)H decoupling. Data for \(^1\)H, \(^{13}\)C, \(^{19}\)F NMR are recorded as follows: chemical shift (\(\delta\), ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet et al.), integration, and coupling constant (Hz). {note: some of the NMR spectra were recorded on Bruker-400 (400 MHz for \(^1\)H; 101 MHz for \(^{13}\)C and 376 MHz for \(^{19}\)F) and Bruker-600 (600 MHz for \(^1\)H; 151 MHz for \(^{13}\)C and 565 MHz for \(^{19}\)F) }. High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight). High performance liquid chromatography was performed on SHIMADZU DGU-20A3R, using IA, IC, AYH, ADH, OJH, ODH, ASH chiral columns eluted with a mixture of hexane/isopropyl alcohol. NiBr\(_2\)·DME and TBAI were obtained from Sigma-Aldrich Chemicals. Mn powder was purchased from Adamas. Anhydrous THF was purchased from J&K Chemicals. N,N-Dimethylpropionamide was obtained from HEOWNS Chemicals. Chiral bisoxazoline ligand, secondary alkyl bromides and vinyl iodides were synthesized via following method described in this supplementary information.
II. Supplementary Methods

Optimization of conditions

**Supplementary Table S1. Optimization of Ligands**

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.10 mmol, 1.0 equiv), NiBr₂-DME (10 mol%), Ligand (13 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.05 mmol, 0.5 equiv), THF (0.5 mL), -4 °C, 20 h. Isolated yield was given. The ee values were determined by HPLC on a chiral stationary phase.
### Supplementary Table S2. Optimization of Solvents

| Entry | Solvent     | Yield (%)<sup>a</sup> | ee (%)<sup>b</sup> |
|-------|-------------|------------------------|--------------------|
| 1     | DMA         | 35                     | 56                 |
| 2     | DMF         | n. d.                  | --                 |
| 3     | CH<sub>3</sub>CN | trace                | --                 |
| 4     | NMP         | n. d.                  | --                 |
| 5     | DME         | 8                      | 82                 |
| 6<sup>c</sup> | 1,4-Dioxane | n. d.                  | --                 |
| 7     | THF         | 37                     | 93                 |

Unless otherwise noted, the reaction conditions were as follows: 1<sub>a</sub> (0.10 mmol, 1.0 equiv), 2<sub>a</sub> (0.10 mmol, 1.0 equiv), NiBr<sub>2</sub>·DME (10 mol%), L8 (13 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.05 mmol, 0.5 equiv), solvent (0.50 mL), -4 °C, 20 h. <sup>a</sup>Isolated yield. <sup>b</sup>The ee values were determined by HPLC on a chiral stationary phase. <sup>c</sup>The reaction was performed under room temperature.
### Supplementary Table S3. Optimization of Ni-Catalysts

| Entry | Ni Source            | Yield (%)<sup>a</sup> | ee (%)<sup>b</sup> |
|-------|----------------------|------------------------|---------------------|
| 1     | NiBr<sub>2</sub>:DME | 37                     | 93                  |
| 2     | NiCl<sub>2</sub>:DME | 31                     | 90                  |
| 3     | NiBr<sub>2</sub>     | trace                  | --                  |
| 4     | NiCl<sub>2</sub>     | n. d.                  | --                  |
| 5     | NiI<sub>2</sub>      | 21                     | 89                  |
| 6     | Ni(OTf)<sub>2</sub>  | trace                  | --                  |
| 7     | Ni(OAc)<sub>2</sub>  | n. d.                  | --                  |

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.10 mmol, 1.0 equiv), Ni Source (10 mol%), L8 (13 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.05 mmol, 0.5 equiv), THF (0.50 mL), -4 °C, 20 h. <sup>a</sup>Isolated yield. <sup>b</sup>The ee values were determined by HPLC on a chiral stationary phase.
**Supplementary Table S4. Quant of 2a**

| Entry | Quant of 2a (equiv) | Yield (%)<sup>a</sup> | ee (%)<sup>b</sup> |
|-------|---------------------|------------------------|-------------------|
| 1     | 1.00                | 37                     | 93                |
| 2     | 1.25                | 41                     | 93                |
| 3     | 1.50                | 45                     | 93                |
| 4     | 1.75                | 46                     | 92                |
| 5     | 2.00                | 51                     | 93                |
| 6     | 2.25                | 51                     | 93                |
| 7     | 2.50                | 50                     | 92                |
| 8     | 3.00                | 48                     | 92                |

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.x mmol, x equiv), NiBr₂·DME (10 mol%), **L8** (13 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.05 mmol, 0.5 equiv), THF (0.50 mL), -4 °C, 20 h. <sup>a</sup> Isolated yield. <sup>b</sup> The ee values were determined by HPLC on a chiral stationary phase.
Supplementary Table S5. Quant of additive

| Entry | Quant of TBAI (equiv) | Yield (%)<sup>a</sup> | ee (%)<sup>b</sup> |
|-------|------------------------|------------------------|-------------------|
| 1     | 0.25                   | 33                     | 91                |
| 2     | 0.50                   | 51                     | 93                |
| 3     | 1.00                   | 59                     | 93                |
| 4     | 1.50                   | 55                     | 92                |

Unless otherwise noted, the reaction conditions were as follows: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.20 mmol, 2.0 equiv), NiBr₂-DME (10 mol%), **L8** (13 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.x mmol, x equiv), THF (0.50 mL), -4 °C, 20 h. <sup>a</sup>Isolated yield. <sup>b</sup>The ee values were determined by HPLC on a chiral stationary phase.
**Supplementary Table S6.** Co-solvent screening and adjustment of ligand

| Entry | Solvent                  | Ligand | Yield (%)<sup>a</sup> | ee (%)<sup>b</sup> |
|-------|--------------------------|--------|------------------------|------------------|
| 1     | DMAc                     | L8     | 78                     | 91               |
| 2     | DMF                      | L8     | n. d.                  | --               |
| 3     | NMP                      | L8     | 65                     | 89               |
| 4     | N,N-Dimethylpropionamide | L8     | 79                     | 92               |
| 5     | N,N-Diethylformamide     | L8     | n. d.                  | --               |
| 6     | N-Acetylmorpholine       | L8     | 64                     | 92               |
| 7     | N,N-Dimethylpropionamide | L9     | 90                     | 95               |

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.20 mmol, 2.0 equiv), NiBr₂-DME (10 mol%), Ligand (13 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.10 mmol, 1.0 equiv), THF (0.45 mL), co-solvent (0.05 ml), -4 °C, 20 h. <sup>a</sup>Isolated yield. <sup>b</sup>The ee values were determined by HPLC on a chiral stationary phase.
General procedure

Synthesis of new chiral bisoxazoline ligands

The ligand L8 was synthesized according to the reported literature with modifications. [1]

The ligand skeleton A (458 mg, 1.0 mmol, 1 equiv.) and tBuOK (112 mg, 1.0 mmol, 1 equiv.) were firstly combined in a 25 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N2 (repeated for 3 times). THF (4 mL) was added to the reaction tube and the mixture was stirred at 40 °C for 1 hour. Then a solution of MeI (62 μL, 1.0 mmol, 1 equiv.) in THF (5 mL) was added dropwise (over 20 min). The resulting mixture was heated to 60 °C and stirred for 4 hours (TLC monitored). The mixture was quenched with sat. NH4Cl solution and extracted with ethyl acetate for three times. The organic layer was combined and washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel (PE/EA = 3/2) to give the desired product B.

The mono methylated ligand B (370 mg, 0.8 mmol, 1 equiv.) was firstly added to a 25 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N2 (repeated for 3 times). THF (8 mL) was added to the reaction tube and the vessel was cooled to -78 °C. n-butyllithium (0.47 mL, 1.12 mmol, 2.4 M in hexane, 1.4 equiv.) was added to the reaction tube dropwise. After that, the reaction was stirred at room temperature for 30 min. Then the reaction tube was transferred to -78 °C and a solution of 1-(Bromomethyl)naphthalene (354 mg, 1.6 mmol, 2 equiv.) in THF (2 mL) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 8 hours. The mixture was quenched with sat. NH4Cl solution and extracted with ethyl acetate for three times. The organic layer was washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel (PE/EA = 3/1) to give the desired product L8.

(4R,4'R,5S,5'S)-2,2’-(1-(naphthalen-1-yl)propane-2,2-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole)

The Ligand L8 was purified with silica gel chromatography as a white solid (318 mg, 52% yield over
two steps); mp: 157-159 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.40 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 6.9 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.07 – 6.90 (m, 20H), 5.84 (dd, J = 10.2, 5.4 Hz, 2H), 5.64 (d, J = 10.1 Hz, 1H), 5.34 (d, J = 10.3 Hz, 1H), 4.31 – 4.18 (m, 2H), 1.89 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.3, 168.7, 137.6, 137.5, 136.3, 136.0, 134.1, 133.4, 133.2, 129.1, 129.0, 128.1, 128.0, 127.8, 127.72, 127.70, 127.65, 127.6, 127.5, 127.1, 127.0, 126.9, 126.8, 125.9, 125.5, 125.4, 124.6, 86.6, 86.3, 73.9, 73.8, 45.1, 37.8, 22.7. HRMS (ESI): m/z calcd. for C₄₃H₇₇N₂O₂⁺ [M + H⁺]: 613.2850, found: 613.2857.

The ligand L₉ was synthesized according to the reported literature with modifications. [2]

One 100 mL, one-necked Schlenk flask was charged with D (3.68 g, 20.0 mmol, 2.0 equiv.) and THF (40 mL) under nitrogen. The solution was cooled to -78 °C, and n-butyllithium (8.3 mL, 2.4 M in hexane, 20.0 mmol, 2.0 equiv.) was added dropwise by syringe. The resulting solution was stirred at -78 °C for 1.5 h. Then compound C (4.35 g, 10.0 mmol, 1.0 equiv.) in THF (15 mL) was added to the organolithium solution using a syringe dropwise over 30 min. The resulting mixture was stirred at -78 °C for 12 h. After that the reaction was quenched by the addition of sat. NH₄Cl solution (20 mL) at -78 °C and slowly warmed to 25 °C. The mixture was transferred to a 250 mL separatory funnel. The aqueous layer was extracted with ethyl acetate (3 × 50 mL), and the organic layers were combined, washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel (PE/EA = 10/1) to give the desired product E (8.0 mmol, 80% yield).

A 250 mL, one-necked Schlenk flask with an eggshaped stir bar was charged with E (8.0 mmol) and methanol (10 mL). HCl solution (60 mL, 6 M in MeOH) was added dropwise by syringe. The reaction was stirred for 2 h at 25 °C, and then the solvent was removed by rotary evaporation. The crude solid was suspended in dichloromethane (50 mL) and 80 mL of NaOH solution (8 M in H₂O) was added while
the solution was stirred vigorously. The solution was stirred for 1 h and then was transferred to a 500 mL separatory funnel. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The organic layers were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by recrystallization (hexane) to give the desired amino alcohol F (6.0 mmol, 75% yield).

The amino alcohol F (6.0 mmol, 2.0 equiv.) and the hydrochloride (3.0 mmol, 1.0 equiv.) was firstly added to a 100 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N₂ (repeated for 3 times). Dichloromethane (30 mL) was added to the reaction tube and stirred at room temperature for 2 days. After that, the reaction was quenched with 20 mL H₂O and extracted with dichloromethane (3 × 20 mL). The organic layers were combined, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by recrystallization (hexane and ethyl acetate) to give the desired skeleton G (2 mmol, 67% yield).

The following steps to synthesize L₉ was similar to L₈.

(4R,4'R,5S,5'S)-2,2'-((1-(naphthalen-1-yl)propane-2,2-diyl)bis(4-(3,5-dimethylphenyl)-5-phenyl-4,5-dihydrooxazole)
Synthesis of Secondary Alkyl Bromides and Alkyl Vinyl Iodides

The substrate $S_1$ was synthesized according to the reported literature. [3]

4-bromo-5,5,5-trifluoropentyl ($E$)-2-(3-(3,4-dimethoxyphenyl)acrylamido)benzoate

The substrate $S_1$ was purified with silica gel chromatography (PE/EA = 7/1) as a white solid (688 mg, 65% yield); mp: 103-104 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 11.20 (s, 1H), 8.86 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.98 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.66 (d, $J = 15.5$ Hz, 1H), 7.54 (ddd, $J = 8.7, 7.3, 1.7$ Hz, 1H), 7.11 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.08–7.04 (m, 2H), 6.83 (d, $J = 8.3$ Hz, 1H), 6.44 (d, $J = 15.4$ Hz, 1H), 4.40–4.32 (m, 2H), 4.21–4.14 (m, 1H), 3.87 (s, 3H), 3.91 (s, 3H), 2.26–2.19 (m, 1H), 2.17–2.10 (m, 1H), 2.05–1.99 (m, 1H), 1.98–1.89 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -72.14 (d, $J = 7.6$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.3, 164.7, 151.0, 149.2, 142.3, 123.9 (q, $J = 277.5$ Hz), 122.6, 122.5, 120.7, 119.5, 114.6, 111.0, 109.7, 63.9, 56.0, 55.9, 46.8 (q, $J = 32.8$ Hz), 28.4, 26.1. HRMS (ESI): m/z calcd. for C$_{23}$H$_{24}$BrF$_3$NO$_5$+$[M + H]^+$: 530.0784, found: 530.0791.

The substrate $S_2$ was synthesized according to the reported literature with modifications. [4]

A mixture of propiolic acid (0.80 ml, 20 mmol, 1.0 equiv.) and aqueous HI (12.0 mL, 7 M aqueous solution, 80 mmol, 4.0 equiv.) was heated in three foil-wrapped Ace tubes at 95 °C for 24 hours. The resulting mixtures were allowed to cool to ambient temperature to afford a suspension of the acid in excess aqueous HI. The pressure was released (CARE), then the mixtures were extracted with dichloromethane (3 × 20 mL). The organic layers were combined, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude (E)-3-iodoacrylic acid was used directly without further purification. To an ice-water cooled solution of (E)-3-iodoacrylic acid (0.8 g, 4 mmol, 1.0 equiv.), piperidine (0.43 mL, 4.4 mmol, 1.1 equiv.), 4-methyl morpholine (0.5 mL, 4.4 mmol, 1.1 equiv.) in DCM (8 mL) was added EDCI (0.9 g, 4.4 mmol, 1.1 equiv.) in small portions. The reaction was stirred at 0 °C for 2 hours. After completion, the solution was washed with diluted hydrochloric acid and water, and then dried with Na$_2$SO$_4$. The crude residue after concentration in vacuo was purified by flash silica gel chromatography (PE/EA = 5/1) to afford $S_2$. 

S13
(E)-3-iodo-1-(piperidin-1-yl)prop-2-en-1-one

The substrate S2 was purified with silica gel chromatography as a yellow oil (763 mg, 72% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.56 (d, $J$ = 14.2 Hz, 1H), 7.25 (d, $J$ = 14.2 Hz, 1H), 3.56 – 3.43 (m, 4H), 1.65 – 1.54 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 163.6, 136.1, 95.1, 47.0, 43.3, 26.7, 25.5, 24.5. HRMS (EI): m/z calcd. for C$_{8}$H$_{12}$INO [M]: 264.9964, found: 264.9966.

The substrate S3, S4, S5 was synthesized according to the reported literature with modifications. [5]

ZrCp$_2$Cl$_2$ (3.2 g, 11 mmol, 1.1 equiv.) in THF (25 mL) cooled to 0 °C was added slowly a solution of DIBAL-H (1.6 g, 11 mmol, 1.1 equiv.) in THF (5 mL) under N$_2$. The resultant suspension was stirred for 30 min at 0 °C, followed by addition of a solution of 3-Butyn-1-ol (0.76 mL, 10 mmol, 1.0 equiv.) in THF (5 mL). The mixture was warmed to room temperature and stirred until a homogeneous solution resulted (ca. 1 h) and then cooled to -78 °C, followed by addition of I$_2$ (3.3 g, 13 mmol, 1.3 equiv.) in THF (15 mL). After 8 h at -78 °C, the reaction mixture was quenched with 1N HCl, extracted with ethyl acetate, washed successively with saturated Na$_2$S$_2$O$_3$, NaHCO$_3$ and brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography (PE/EA = 10/1) to give the desired alcohol (3.1 mmol, 31% yield).

To an anhydrous THF (12 mL) solution of acid (3.0 mmol, 1.0 equiv.), (E)-4-iodo-3-buten-1-ol (0.59 g, 3.0 mmol, 1.0 equiv.) and triphenylphosphine (0.87 g, 3.3 mmol, 1.1 equiv.) was slowly added a THF solution (5 mL) of diethyl azodicarboxylate (0.52 mL, 3.3 mmol, 1.1 equiv.) over 30 min at 0 °C. The resulting mixture was then stirred at room temperature for 12 hours. The reaction was quenched with saturated NaCl solution (15 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated. The residue was purified with flash chromatography on silica gel to give the desired product.

(E)-4-iobutan-3-yn-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate
The substrate S3 was purified with silica gel chromatography (PE/EA = 10/1) as a white solid (926 mg, 62% yield); mp: 105-107 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.76 – 7.69 (m, 4H), 7.45 – 7.43 (m, 2H), 6.86 – 6.83 (m, 2H), 6.33 (dt, $J = 14.4, 7.2$ Hz, 1H), 6.06 (dt, $J = 14.4, 1.4$ Hz, 1H), 4.20 (t, $J = 6.3$ Hz, 2H), 6.06 (dt, $J = 14.4, 1.4$ Hz, 1H), 1.67 (s, 6H). 13C NMR (126 MHz, CDCl$_3$) δ 194.3, 173.7, 159.7, 141.2, 138.5, 136.5, 132.3, 131.3, 130.6, 128.7, 117.3, 79.4, 78.0, 63.5, 35.1, 25.6. HRMS (ESI): m/z calcd. for C$_{21}$H$_{21}$ClIO$_4$ $^+$ [M + H$^+$]: 499.0168, found: 499.0180.

(E)-7-phenyl-5-(trifluoromethyl)hept-3-en-1-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate

The substrate S4 was purified with silica gel chromatography (PE/EA = 20/1) as a colorless oil (623 mg, 49% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.57 – 7.54 (m, 2H), 7.46 – 7.40 (m, 3H), 7.38 – 7.35 (m, 1H), 7.16 – 7.10 (m, 2H), 6.42 (dt, $J = 14.4, 7.2$ Hz, 1H), 6.05 (dt, $J = 14.4, 1.4$ Hz, 1H), 4.19 – 4.09 (m, 2H), 3.75 (q, $J = 7.1$ Hz, 1H), 2.37 – 2.33 (m, 2H), 1.54 (d, $J = 7.2$ Hz, 3H). 19F NMR (471 MHz, CDCl$_3$) δ -117.38 – -117.43 (m). 13C NMR (126 MHz, CDCl$_3$) δ 173.9, 159.8 (d, $J = 248.3$ Hz), 141.7 (d, $J = 8.1$ Hz), 141.6, 135.6, 131.0 (d, $J = 3.8$ Hz), 129.1 (d, $J = 2.8$ Hz), 128.6, 128.0 (d, $J = 13.8$ Hz), 127.8, 123.7 (d, $J = 3.6$ Hz), 115.4 (d, $J = 23.7$ Hz), 77.7, 62.8, 45.1, 35.3, 18.3. HRMS (ESI): m/z calcd. for C$_{19}$H$_{18}$FINaO$_2$ $^+$ [M + Na$^+$]: 447.0228, found: 447.0232.

(E)-4-iodobut-3-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

The substrate S5 was purified with silica gel chromatography (PE/EA = 3/1) as a yellow solid (1.03 g, 64% yield); mp: 60-62 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.69 – 7.65 (m, 2H), 7.48 – 7.45 (m, 2H), 6.95 (d, $J = 2.6$ Hz, 1H), 6.86 (d, $J = 9.0$ Hz, 1H), 6.67 (dd, $J = 9.0, 2.6$ Hz, 1H), 6.42 (dt, $J = 14.4, 7.1$ Hz, 1H), 6.05 (dt, $J = 14.5, 1.4$ Hz, 1H), 4.13 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 3.66 (s, 2H), 2.39 – 2.33 (m, 5H). 13C NMR (126 MHz, CDCl$_3$) δ 170.8, 168.4, 156.2, 141.6, 139.3, 136.1, 134.0, 131.3, 130.9, 130.7, 129.2, 115.1, 112.5, 111.7, 101.4, 77.6, 62.9, 55.9, 35.3, 30.4, 13.5. HRMS (ESI): m/z calcd. for C$_{23}$H$_{23}$CHINaO$_2$ $^+$ [M + Na$^+$]: 560.0096, found: 560.0107.
The substrate S6 was synthesized according to the reported literature. \(^6\)

Iodine (685 mg, 2.7 mmol, 2.7 equiv) was added to a solution of alcohol (234 mg, 1.0 mmol, 1.0 equiv), PPh_3 (917 mg, 3.5 mmol, 3.5 equiv) and imidazole (184 mg, 2.7 mmol, 2.7 equiv) in toluene (10 mL). The resulting mixture was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction was quenched with water. The aqueous phase was extracted with ethyl acetate for three times. The combined organic layers were washed with saturated Na_2S_2O_3 and brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography on silica gel to give desired fluorinated alkyl iodide.

**1-methoxy-4-(4,4,4-trifluoro-3-iodobutyl)benzene**

The substrate S6 was purified with silica gel chromatography (PE/EA = 50/1) as a colorless oil (210 mg, 61% yield). \(^1\)H NMR (500 MHz, CDCl_3) \(\delta\) 7.16 – 7.13 (m, 2H), 6.89 – 6.85 (m, 2H), 4.05 – 3.98 (m, 1H), 3.81 (s, 3H), 2.93 (dt, \(J = 13.3, 6.3\) Hz, 1H), 2.64 (dt, \(J = 14.0, 8.2\) Hz, 1H), 2.14 (td, \(J = 8.1, 6.5\) Hz, 2H). \(^19\)F NMR (471 MHz, CDCl_3) \(\delta\) -68.70 (d, \(J = 7.2\) Hz). \(^13\)C NMR (126 MHz, CDCl_3) \(\delta\) 158.5, 131.2, 129.6, 124.8 (q, \(J = 276.5\) Hz), 114.3, 55.4, 34.5, 33.6, 23.8 (q, \(J = 31.0\) Hz). HRMS (ESI): m/z calcd. for C_{11}H_{13}F_{3}IO\(^{+}\) [M + H\(^{+}\)]: 344.9958, found: 344.9945.
General Procedure for Nickel-catalyzed Asymmetric Reductive Trifluoroalkylation of Vinyl Iodides

NiBr₂•DME (10 mol%, 0.01 mmol, 3.1 mg), L9 (13 mol%, 0.013 mmol, 8.7 mg), Mn powder (2.0 equiv, 0.20 mmol, 11.0 mg), TBAI (1.0 equiv, 0.10 mmol, 36.9 mg) and vinyl iodide 1 (1.0 equiv, 0.10 mmol) were firstly combined in a 10 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N₂ (repeated for 3 times). Alkyl bromide 2 (2.0 equiv, 0.20 mmol), THF (0.45 mL) and N,N-Dimethylpropionamide (0.05 mL) were added via syringe. The tube was sealed with a Teflon lined cap and stirred at -4 °C for 20 h. The reaction mixture was then diluted with ethyl acetate (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with ethyl acetate (3 × 15 mL), the combined organic layer was dried over Na₂SO₄, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired products.

**methyl (E)-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzoate**

The product 3 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (31.2 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 6.8 Hz, 2H), 6.61 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.9, 9.3 Hz, 1H), 3.94 (s, 3H), 2.94 – 2.87 (m, 1H), 2.84 – 2.78 (m, 1H), 2.64 – 2.58 (m, 1H), 2.25 – 2.18 (m, 1H), 1.98 – 1.90 (m, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -70.43 (d, J = 8.6 Hz). ¹³C NMR (126 MHz, CDCl₃) δ 166.9, 140.6, 140.6, 135.6, 130.1, 129.7, 128.7, 128.5, 126.9 (q, J = 280.7 Hz) 126.5, 126.4, 125.4 (q, J = 2.7 Hz), 52.2, 47.3 (q, J = 26.8 Hz), 32.5, 29.4. HRMS (ESI): m/z calcd. for C₂₀H₂₅F₃O₂⁺ [M + H⁺]: 349.1410, found: 349.1410. [α]D²⁰ = 1.2 (c = 1.0, CHCl₃), HPLC chiralcel OD-H column (2% isopropanol in hexanes, 0.5 mL/min, λ = 254 nm), tₓ = 35.1 min (minor), 39.5 min (major), 95% ee.

**methyl (E)-3-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzoate**
The product 4 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (26.9 mg, 77% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (t, $J = 1.8$ Hz, 1H), 7.96 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.59 (dt, $J = 7.7$, 1.6 Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.31 (t, $J = 7.4$ Hz, 2H), 7.24 – 7.17 (m, 3H), 6.60 (d, $J = 15.9$ Hz, 1H), 6.10 (dd, $J = 15.9$, 9.4 Hz, 1H), 3.95 (s, 3H), 2.94 – 2.76 (m, 2H), 2.63 – 2.56 (m, 1H), 2.23 – 2.15 (m, 1H), 1.97 – 1.87 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.58 (d, $J = 8.8$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.0, 140.7, 140.6, 136.7, 135.5, 131.0, 130.8, 129.3, 128.9, 128.7, 128.6, 127.6, 126.9 (q, $J = 280.8$ Hz), 126.4, 124.1 (q, $J = 2.6$ Hz), 52.4, 47.3 (q, $J = 26.8$ Hz), 32.6, 29.4 (q, $J = 2.0$ Hz).

HRMS (EI): m/z calcd. for C$_{20}$H$_{19}$F$_3$O$_2$ [M]: 348.1337, found: 348.1330. [$\alpha$]$_{D}^{20}$ = 0.3 (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (4% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R$ = 7.0 min (minor), 8.4 min (major), 94% ee.

(E)-1-(4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)phenyl)ethan-1-one

The product 5 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (27.6 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.15 (m, 3H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.14 (dd, $J = 15.9$, 9.4 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.83 – 2.76 (m, 1H), 2.65 – 2.56 (m, 4H), 2.24 – 2.16 (m, 1H), 1.98 – 1.88 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.44 (d, $J = 8.4$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.6, 140.8, 140.6, 136.7, 135.5, 129.0, 128.7, 128.5, 126.8 (q, $J = 280.5$ Hz), 126.8, 126.5, 125.7 (q, $J = 2.4$ Hz), 47.3 (q, $J = 27.0$ Hz), 32.6, 29.4, 26.8. HRMS (ESI): m/z calcd. for C$_{20}$H$_{19}$F$_3$O$_2$$^+$ [M + H$^+$]: 333.1461, found: 333.1461. [$\alpha$]$_{D}^{20}$ = 2.4 (c = 2.0, CHCl$_3$), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R$ = 10.1 min (minor), 15.4 min (major), 95% ee.

(E)-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzonitrile
The product 6 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (27.1 mg, 86% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, $J$ = 8.4 Hz, 2H), 7.48 (d, $J$ = 8.4 Hz, 2H), 7.31 (t, $J$ = 7.5 Hz, 2H), 7.22 (t, $J$ = 7.4 Hz, 1H), 7.17 (d, $J$ = 6.7 Hz, 2H), 6.57 (d, $J$ = 15.9 Hz, 1H), 6.14 (dd, $J$ = 15.9, 9.4 Hz, 1H), 2.98 – 2.83 (m, 1H), 2.81 – 2.75 (m, 1H), 2.62 – 2.56 (m, 1H), 2.24 – 2.17 (m, 1H), 1.96 – 1.88 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.40 (d, $J$ = 8.5 Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.6, 140.4, 134.9, 132.7, 128.8, 128.5, 127.2, 126.8 (q, $J$ = 2.9 Hz), 126.7 (q, $J$ = 280.7 Hz) 126.5, 118.9, 111.6, 47.3 (q, $J$ = 26.9 Hz). HRMS (ESI): m/z calcd. for C$_{19}$H$_{17}$F$_3$N$^+$ [M + H$^+$]: 316.1308, found: 316.1335. [$\alpha$]$_D^{20}$ = 1.0 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (4% isopropanol in hexanes, 1.0 mL/min, $\lambda$ = 254 nm), t$_R$ = 15.0 min (minor), 20.3 min (major), 95% ee.

(E)-1-fluoro-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

The product 7 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (24.6 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.14 (m, 3H), 7.10 – 7.00 (m, 2H), 6.53 (d, $J$ = 15.9 Hz, 1H), 5.92 (dd, $J$ = 15.8, 9.4 Hz, 1H), 2.91 – 2.76 (m, 2H), 2.63 – 2.55 (m, 1H), 2.22 – 2.13 (m, 1H), 1.94 – 1.85 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.67 (d, $J$ = 9.4 Hz), -113.50 – -113.58 (m). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 162.8 (d, $J$ = 247.6 Hz), 140.7, 135.3, 132.5 (q, $J$ = 3.2 Hz), 128.7, 128.6, 128.2 (d, $J$ = 7.9 Hz), 127.0 (d, $J$ = 279.9 Hz), 126.4, 122.5, 115.8 (d, $J$ = 21.6 Hz), 47.2 (q, $J$ = 26.7 Hz), 32.6, 29.4. HRMS (EI): m/z calcd. for C$_{18}$H$_{16}$F$_4$ [M]: 308.1188, found: 308.1187. [$\alpha$]$_D^{20}$ = 1.3 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda$ = 254 nm), t$_R$ = 7.1 min (minor), 8.5 min (major), 94% ee.

(E)-1-chloro-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

The product 8 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (17.3 mg, 53% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.27 (m, 6H), 7.24 – 7.20 (m, 1H), 7.19 – 7.16 (m, 2H), 6.52 (d, $J$ = 15.8 Hz, 1H), 5.98 (dd, $J$ = 15.9, 9.3 Hz, 1H), 2.91 – 2.75 (m, 2H), 2.63 – 2.55 (m, 1H), 2.22 – 2.14 (m, 1H), 1.95 – 1.85 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.60 (d, $J$ = 8.2 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.7, 135.3, 134.8, 134.0, 129.0, 128.7, 128.5, 127.9, 126.9 (q, $J$ = 280.8
Hz), 126.4, 123.4 (q, $J = 2.7$ Hz), 47.3 (q, $J = 26.8$ Hz), 32.6, 29.4 (q, $J = 2.1$ Hz). HRMS (EI): $m/z$ calcd. for C$_{18}$H$_{16}$ClF$_3$ [M]: 324.0893, found: 324.0891. $[^{19}S]D_{20}^2 = 1.8$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 8.0$ min (minor), 9.3 min (major), 94% ee.

$(E)$-1-chloro-3-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

![Product 9](image)

The product 9 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (28.1 mg, 87% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 – 7.40 (m, 1H), 7.33 – 7.29 (m, 2H), 7.28 – 7.25 (m, 3H), 7.26 – 7.19 (m, 1H), 7.21 – 7.15 (m, 2H), 6.51 (d, $J = 15.8$ Hz, 1H), 6.03 (dd, $J = 15.9$, 9.3 Hz, 1H), 2.90 – 2.76 (m, 2H), 2.62 – 2.55 (m, 1H), 2.22 – 2.15 (m, 1H), 1.94 – 1.87 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.57 (d, $J = 8.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.6, 138.1, 135.2, 134.8, 130.1, 128.7, 128.6, 128.3, 126.9 (q, $J = 280.1$ Hz), 126.6, 126.5, 124.9, 124.3 (q, $J = 2.7$ Hz), 47.2 (q, $J = 26.8$ Hz), 32.5, 29.4. HRMS (EI): $m/z$ calcd. for C$_{18}$H$_{16}$ClF$_3$ [M]: 324.0893, found: 324.0893. $[^{19}S]D_{20}^2 = 1.9$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (1% isopropanol in hexanes, 0.5 mL/min, $\lambda = 254$ nm), $t_R = 9.7$ min (minor), 11.2 min (major), 94% ee.

$(E)$-1-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)-4-(trifluoromethyl)benzene

![Product 10](image)

The product 10 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (28.0 mg, 78% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 8.1$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.18 (m, 2H), 6.60 (d, $J = 15.8$ Hz, 1H), 6.12 (dd, $J = 15.9$, 9.4 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.83 – 2.77 (m, 1H), 2.64 – 2.58 (m, 1H), 2.25 – 2.18 (m, 1H), 1.97 – 1.89 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.58, -70.51 (d, $J = 8.2$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.6, 139.7, 135.2, 130.2 (q, $J = 32.3$ Hz), 128.8, 128.6, 126.9, 126.9 (q, $J = 280.4$ Hz), 126.5, 125.8 (q, $J = 3.7$ Hz), 125.5 (q, $J = 2.7$ Hz), 124.2 (q, $J = 271.8$ Hz), 47.3 (q, $J = 27.0$ Hz), 32.6, 29.4. HRMS (EI): $m/z$ calcd. for C$_{19}$H$_{16}$F$_6$ [M]: 358.1156, found: 358.1154. $[^{19}S]D_{20}^2 = 0.8$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 6.6$ min (minor), 8.1 min (major), 95% ee.
**(E)-1-methoxy-4-(5-phenyl-3-( trifluoromethyl)pent-1-en-1-yl)benzene**

![Image of compound 11]

The product 11 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (17.1 mg, 53% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 – 7.33 (m, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.13 (m, 3H), 6.95 – 6.83 (m, 2H), 6.51 (d, $J = 15.8$ Hz, 1H), 5.86 (dd, $J = 15.8$, 9.3 Hz, 1H), 3.83 (s, 3H), 2.85 – 2.76 (m, 2H), 2.69 – 2.50 (m, 1H), 2.19 – 2.12 (m, 1H), 1.92 – 1.84 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.74. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.7, 140.9, 135.9, 129.1, 128.7, 128.6, 127.9, 127.1 (q, $J = 280.5$ Hz), 126.3, 120.4 (q, $J = 2.5$ Hz), 114.2, 55.5, 47.3 (q, $J = 26.5$ Hz), 32.6, 29.6. HRMS (EI): m/z calcd. for C$_{19}$H$_{19}$F$_3$O [M]: 320.1388, found: 320.1383. $[^{[\alpha]}]_{D}^{20} = 1.2$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (2% isopropanol in hexanes, 0.5 mL/min, $\lambda = 254$ nm), $t_R$ = 15.1 min (minor), 20.7 min (major), 88% ee.

**(E)-1-methoxy-3-(5-phenyl-3-( trifluoromethyl)pent-1-en-1-yl)benzene**

![Image of compound 12]

The product 12 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (28.3 mg, 88% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33 – 7.26 (m, 3H), 7.24 – 7.16 (m, 3H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 2.0$ Hz, 1H), 6.86 (ddd, $J = 8.2$, 2.6, 0.9 Hz, 1H), 6.55 (d, $J = 15.8$ Hz, 1H), 6.01 (dd, $J = 15.8$, 9.3 Hz, 1H), 3.85 (s, 3H), 2.90 – 2.77 (m, 2H), 2.62 – 2.56 (m, 1H), 2.21 – 2.14 (m, 1H), 1.94 – 1.86 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.62 (d, $J = 8.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.0, 140.8, 137.7, 136.4, 129.8, 128.7, 128.6, 127.0 (q, $J = 280.1$ Hz), 126.4, 123.0 (q, $J = 2.8$ Hz), 119.3, 113.9, 112.0, 55.4, 47.2 (q, $J = 26.7$ Hz), 32.5, 29.5. HRMS (ESI): m/z calcd. for C$_{19}$H$_{20}$F$_3$O$^+$ [M + H$^+$]: 321.1461, found: 321.1438. $[^{[\alpha]}]_{D}^{20} = 0.9$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (2% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R$ = 5.6 min (minor), 6.7 min (major), 94% ee.

**(E)-(3-( trifluoromethyl)pent-1-ene-1,5-diyl)dibenzene**

![Image of compound 13]
The product 13 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (18.9 mg, 65% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.40 (m, 2H), 7.41 – 7.34 (m, 2H), 7.34 – 7.29 (m, 3H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.02 (dd, $J = 15.9$, 9.4 Hz, 1H), 2.92 – 2.77 (m, 2H), 2.64 – 2.56 (m, 1H), 2.25 – 2.14 (m, 1H), 1.96 – 1.86 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.65 (d, $J = 8.8$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.8, 136.5, 136.3, 128.8, 128.7, 128.6, 128.3, 127.0 (q, $J = 280.9$ Hz), 126.7, 126.4, 122.7 (q, $J = 2.6$ Hz), 47.3 (q, $J = 26.6$ Hz), 32.6, 29.5 (q, $J = 2.0$ Hz). HRMS (EI): m/z calcd. for C$_{18}$H$_{17}$F$_{3}$ [M]: 290.1282, found: 290.1283. $[^{[\alpha]}D]_{20}^0 = 0.4$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_{R}$ = 7.1 min (major), 9.4 min (minor), 92% ee.

$^{(E)}$-2-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)naphthalene

![Structure 14]

The product 14 was purified with silica gel chromatography (PE/EA = 60/1) as a white solid (18.7 mg, 55% yield); mp: 49-50°C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 – 7.82 (m, 3H), 7.77 (s, 1H), 7.63 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.21 (m, 3H), 6.74 (d, $J = 15.8$ Hz, 1H), 6.14 (dd, $J = 15.8$, 9.4 Hz, 1H), 2.97 – 2.89 (m, 1H), 2.88 – 2.81 (m, 1H), 2.66 – 2.60 (m, 1H), 2.25 – 2.18 (m, 1H), 1.99 – 1.94 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.56 (d, $J = 8.8$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.8, 136.6, 133.7, 133.6, 133.3, 128.7, 128.6, 128.5, 128.2, 127.9, 127.1 (q, $J = 280.5$ Hz), 126.8, 126.6, 126.4, 126.3, 123.5, 123.0 (q, $J = 2.7$ Hz), 47.4 (q, $J = 26.7$ Hz), 32.6, 29.5. HRMS (ESI): m/z calcd. for C$_{22}$H$_{26}$F$_{3}$ [M + H$^+$]: 341.1512, found: 341.1519. $[^{[\alpha]}D]_{20}^0 = 0.2$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (2% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_{R}$ = 11.7 min (minor), 21.6 min (major), 96% ee.

$^{(E)}$-1-methyl-2-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

![Structure 15]

The product 15 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (20.6 mg, 68% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 – 7.46 (m, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.26 – 7.18 (m, 6H), 6.80 (d, $J = 15.8$ Hz, 1H), 5.90 (dd, $J = 15.7$, 9.4 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.66 – 2.60 (m, 1H), 2.39 (s, 3H), 2.24 – 2.16 (m, 1H), 1.96 – 1.89 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.71 (d, $J = 9.5$ Hz, 1H).
Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.8, 135.7, 135.6, 134.6, 130.5, 128.7, 128.6, 128.2, 127.0 (q, $J$ = 280.4 Hz), 126.40, 126.35, 126.1, 124.2 (q, $J$ = 2.6 Hz), 47.4 (q, $J$ = 26.7 Hz), 32.6, 29.4 (q, $J$ = 1.9 Hz), 19.9. HRMS (EI): m/z calcd. for C$_{19}$H$_{19}$F$_3$ [M]: 304.1439, found: 304.1439. 

$[\alpha]_D^{20} = 1.2$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 0.5 mL/min, $\lambda$ = 254 nm), $t_R = 14.3$ min (major), 15.7 min (minor), 95% ee.

(E)-1-methyl-3-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

The product 16 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (16.0 mg, 53% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33 – 7.31 (m, 2H), 7.27 – 7.21 (m, 4H), 7.19 (d, $J$ = 6.9 Hz, 2H), 7.12 (d, $J$ = 7.2 Hz, 1H), 6.55 (d, $J$ = 15.8 Hz, 1H), 6.00 (dd, $J$ = 15.8, 9.3 Hz, 1H), 2.90 – 2.77 (m, 2H), 2.62 – 2.56 (m, 1H), 2.38 (s, 3H), 2.21 – 2.14 (m, 1H), 1.94 – 1.86 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.68 (d, $J$ = 8.7 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.9, 138.4, 136.4, 136.3, 129.1, 128.72, 128.68, 128.6, 127.3, 127.1 (q, $J$ = 280.4 Hz), 126.4, 123.9, 122.5 (q, $J$ = 2.6 Hz), 47.3 (q, $J$ = 26.7 Hz), 32.6, 29.5 (q, $J$ = 2.6 Hz), 21.5. HRMS (EI): m/z calcd. for C$_{19}$H$_{19}$F$_3$ [M]: 304.1439, found: 304.1438. 

$[\alpha]_D^{20} = 0.8$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (1% isopropanol in hexanes, 0.5 mL/min, $\lambda$ = 254 nm), $t_R = 8.6$ min (minor), 9.7 min (major), 93% ee.

(E)-1-methyl-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

The product 17 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (17.7 mg, 58% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.27 (m, 4H), 7.22 (t, $J$ = 7.4 Hz, 1H), 7.18 (t, $J$ = 6.9 Hz, 4H), 6.54 (d, $J$ = 15.8 Hz, 1H), 5.96 (dd, $J$ = 15.8, 9.3 Hz, 1H), 2.89 – 2.77 (m, 2H), 2.62 – 2.56 (m, 1H), 2.37 (s, 3H), 2.20 – 2.14 (m, 1H), 1.93 – 1.85 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.71 (d, $J$ = 8.8 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.9, 138.2, 136.4, 133.6, 129.5, 128.7, 128.6, 127.1 (q, $J$ = 280.4 Hz), 126.6, 126.3, 121.7 (q, $J$ = 2.6 Hz), 47.3 (q, $J$ = 26.7 Hz), 32.6, 29.6 (q, $J$ = 2.3 Hz), 21.4. HRMS (EI): m/z calcd. for C$_{19}$H$_{19}$F$_3$ [M]: 304.1439, found: 304.1435. 

$[\alpha]_D^{20} = 1.7$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (0.4% isopropanol in hexanes, 0.3 mL/min, $\lambda$ = 254 nm), $t_R = 21.2$ min (major), 23.6 min (minor), 93% ee.
(E)-1-(tert-butyl)-4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)benzene

The product 18 was purified with silica gel chromatography (PE/EA = 100/1) as a colorless oil (23.5 mg, 68% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 – 7.34 (m, 4H), 7.31 (t, $J$ = 7.5 Hz, 2H), 7.22 (t, $J$ = 7.4 Hz, 1H), 7.18 (d, $J$ = 6.7 Hz, 2H), 6.56 (d, $J$ = 15.8 Hz, 1H), 5.98 (dd, $J$ = 15.9, 9.3 Hz, 1H), 2.89 – 2.76 (m, 2H), 2.61 – 2.55 (m, 1H), 2.20 – 2.13 (m, 1H), 1.93 – 1.85 (m, 1H), 1.34 (s, 9H). $^1$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.73 (d, $J$ = 8.7 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.5, 140.9, 136.3, 133.6, 128.7, 128.6, 127.1 (q, $J$ = 280.6 Hz), 126.40, 126.35, 125.8, 121.9 (q, $J$ = 2.7 Hz), 47.3 (q, $J$ = 26.8 Hz), 34.8, 32.5, 31.4, 29.5. HRMS (EI): m/z calcd. for C$_{22}$H$_{25}$F$_3$ [M]: 346.1908, found: 346.1907. $[^{10}]$D = 0.7 (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ = 4.8 min (minor), 5.4 min (major), 92% ee.

(E)-(3-(trifluoromethyl)undec-4-en-1-yl)benzene

The product 19 was purified with silica gel chromatography (Hexane) as a colorless oil (12.0 mg, 40% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 (t, $J$ = 7.5 Hz, 2H), 7.25 – 7.15 (m, 3H), 5.68 (dt, $J$ = 15.3, 6.8 Hz, 1H), 5.27 (dd, $J$ = 15.3, 9.2 Hz, 1H), 2.79 – 2.73 (m, 1H), 2.69 – 2.59 (m, 1H), 2.56 – 2.50 (m, 1H), 2.13 – 2.02 (m, 3H), 1.80 – 1.72 (m, 1H), 1.47 – 1.39 (m, 2H), 1.37 – 1.28 (m, 6H), 0.91 (t, $J$ = 6.7 Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -71.17 (d, $J$ = 8.6 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.2, 138.4, 128.6, 127.2 (q, $J$ = 280.0 Hz), 126.3, 123.1 (q, $J$ = 2.7 Hz), 47.0 (q, $J$ = 26.3 Hz), 32.7, 32.5, 31.8, 29.4, 29.1, 28.9, 22.8, 14.2. HRMS (EI): m/z calcd. for C$_{18}$H$_{25}$F$_3$ [M]: 298.1908, found: 298.1904. $[^{10}]$D = 0.1 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (0.5% isopropanol in hexanes, 0.5 mL/min, $\lambda$ = 214 nm), $t_R$ = 9.1 min (minor), 9.8 min (major), 92% ee.

(E)-(5-cyclohexyl-3-(trifluoromethyl)pent-4-en-1-yl)benzene
The product 20 was purified with silica gel chromatography (Hexane) as a colorless oil (9.8 mg, 33% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.19 (m, 1H), 7.17 (d, $J = 7.5$ Hz, 2H), 5.62 (dd, $J = 15.5, 6.7$ Hz, 1H), 5.22 (ddd, $J = 15.5, 9.3, 1.4$ Hz, 1H), 2.77 – 2.72 (m, 1H), 2.65 – 2.49 (m, 2H), 2.09 – 2.00 (m, 2H), 1.80 – 1.65 (m, 6H), 1.36 – 1.26 (m, 2H), 1.23 – 1.08 (m, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -71.21 (d, $J = 8.9$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.1, 141.1, 128.61, 128.58, 127.2 (q, $J = 280.6$ Hz), 126.3, 120.5 (q, $J = 2.5$ Hz), 46.9 (q, $J = 26.3$ Hz), 40.9, 32.93, 32.85, 32.5, 29.4 (q, $J = 1.9$ Hz), 26.2, 26.1. HRMS (EI): m/z calcd. for C$_{18}$H$_{23}$F$_3$ [M]: 296.1752, found: 296.1749.

$[\alpha]_D^{20} = 0.1$ (c = 1.0, CHCl$_3$), HPLC chiralcel O-D column (0.4% isopropanol in hexanes, 0.3 mL/min, $\lambda = 214$ nm), $t_R = 17.0$ min (minor), 17.9 min (major), 88% ee.

(E)-5-(trifluoromethyl)hept-3-ene-1,7-diyldibenzene

The product 21 was purified with silica gel chromatography (Hexane) as a colorless oil (18.5 mg, 58% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.28 (m, 4H), 7.23 – 7.18 (m, 4H), 7.13 (d, $J = 6.9$ Hz, 2H), 5.70 (dt, $J = 15.4, 6.8$ Hz, 1H), 5.28 (ddt, $J = 15.4, 9.2, 1.5$ Hz, 1H), 2.81 – 2.71 (m, 2H), 2.69 – 2.57 (m, 2H), 2.51 – 2.40 (m, 3H), 2.06 – 1.99 (m, 1H), 1.76 – 1.68 (m, 1H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -71.09 (d, $J = 8.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.5, 141.1, 137.1, 128.63, 128.60, 128.56, 128.5, 127.1 (q, $J = 280.0$ Hz), 126.3, 126.1, 124.1 (q, $J = 2.5$ Hz), 46.9 (q, $J = 26.7$ Hz), 35.6, 34.3, 32.5, 29.4 (q, $J = 2.2$ Hz). HRMS (EI): m/z calcd. for C$_{20}$H$_{21}$F$_3$ [M]: 318.1595, found: 318.1590. $[\alpha]_D^{20} = 0.3$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda = 214$ nm), $t_R = 8.0$ min (minor), 9.6 min (major), 92% ee.

ethyl (E)-6-phenyl-4-(trifluoromethyl)hex-2-enoate

The product 22 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (11.7 mg, 41% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 (dd, $J = 8.1, 6.9$ Hz, 2H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 6.9$ Hz, 2H), 6.75 (dd, $J = 15.7, 9.5$ Hz, 1H), 6.01 (d, $J = 15.7$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 2.92 – 2.82 (m, 1H), 2.77 – 2.72 (m, 1H), 2.54 (dt, $J = 13.9, 8.3$ Hz, 1H), 2.19 – 2.12 (m, 1H), 1.93 – 1.86 (m, 1H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.02 (d, $J = 8.2$ Hz). $^{13}$C NMR
(101 MHz, CDCl$_3$) δ 165.5, 140.2, 140.1 (q, $J = 2.5$ Hz), 128.8, 128.5, 127.5, 126.6, 126.2 (q, $J = 280.6$ Hz), 61.0, 46.2 (q, $J = 27.1$ Hz), 32.4, 29.0 (q, $J = 2.3$ Hz), 14.3. HRMS (ESI): m/z calcd. for C$_{15}$H$_{17}$F$_3$NaO$_2$ [M + Na$^+$]: 309.1073, found: 309.1083. [α]$^\text{D}$$^\text{o}$ = 0.2 (c = 0.5, CHCl$_3$), HPLC chiralcel OD-H column (5% isopropanol in hexanes, 1.0 mL/min, $\lambda = 214$ nm), $t_R$ = 6.1 min (minor), 6.7 min (major), 97% ee.

(E)-6-phenyl-1-(piperidin-1-yl)-4-(trifluoromethyl)hex-2-en-1-one

The product 23 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (17.2 mg, 53% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 2H), 6.62 (dd, $J = 15.2$, 9.4 Hz, 1H), 6.42 (d, $J = 15.2$ Hz, 1H), 3.63 (t, $J = 5.4$ Hz, 2H), 3.47 (t, $J = 5.4$ Hz, 2H), 2.91 – 2.73 (m, 2H), 2.58 – 2.50 (m, 1H), 2.19 – 2.10 (m, 1H), 1.95 – 1.85 (m, 1H), 1.75 – 1.65 (m, 3H), 1.62 – 1.57 (m, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.12 (d, $J = 8.3$ Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.1, 140.4, 136.8, 128.7, 128.5, 126.9, 126.47, 126.47 (q, $J = 280.0$ Hz), 47.1, 46.5 (q, $J = 27.0$ Hz), 43.3, 32.4, 29.0, 26.8, 25.6, 24.6. HRMS (EI): m/z calcd. for C$_{18}$H$_{22}$F$_3$NO [M]: 325.1653, found: 325.1656. [α]$^\text{D}$$^\text{20}$ = 0.4 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 214$ nm), $t_R$ = 7.5 min (major), 8.4 min (minor), 93% ee.

(E)-(3-(trifluoromethyl)hex-4-ene-1,5-diyl)dibenzene

The product 24 was purified with silica gel chromatography (Hexane) as a colorless oil (13.7 mg, 45% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 3H), 7.22 – 7.15 (m, 3H), 5.57 (dd, $J = 10.0$, 1.7 Hz, 1H), 3.17 – 3.04 (m, 1H), 2.82 – 2.75 (m, 1H), 2.61 – 2.54 (m, 1H), 2.23 – 2.15 (m, 1H), 1.99 (s, 1H), 1.92 – 1.83 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.44 (d, $J = 9.0$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.1, 141.9, 140.9, 128.7, 128.6, 128.5, 127.7, 127.4 (q, $J = 270.7$ Hz), 126.4, 126.1, 121.5 (q, $J = 2.4$ Hz), 42.6 (q, $J = 26.7$ Hz), 32.6, 30.2 (q, $J = 1.9$ Hz), 16.9. HRMS (EI): m/z calcd. for C$_{19}$H$_{19}$F$_3$ [M]: 304.1439, found: 304.1431. [α]$^\text{D}$$^\text{20}$ = 1.6 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 0.5 mL/min, $\lambda = 214$ nm), $t_R$ = 10.6 min (major), 11.3 min (minor), 93% ee.
The product 25 was purified with silica gel chromatography (Hexane) as a colorless oil (11.7 mg, 32% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.34 (m, 3H), 7.32 – 7.13 (m, 10H), 7.06 – 7.04 (m, 2H), 5.96 (d, $J$ = 10.6 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.75 – 2.67 (m, 1H), 2.43 – 2.35 (m, 1H), 2.09 – 2.00 (m, 1H), 1.88 – 1.79 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -69.75 (d, $J$ = 9.3 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.9, 141.5, 141.2, 139.1, 129.8, 128.7, 128.6, 128.4, 128.1, 127.7, 127.5, 127.3 (q, $J$ = 281.2 Hz), 126.2, 122.0 (q, $J$ = 2.5 Hz), 44.0 (q, $J$ = 26.4 Hz), 32.8, 30.8 (q, $J$ = 2.0 Hz). HRMS (EI): m/z calcd. for C$_{24}$H$_{21}$F$_3$ [M]: 366.1595, found: 366.1596. [$\alpha$]$_D^{20}$ = 0.6 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 1.0 mL/min, $\lambda$ = 214 nm), $t_R$ = 4.9 min (major), 5.5 min (minor), 81% ee.

methyl (E)-4-(4,4,4-trifluoro-3-methylbut-1-en-1-yl)benzoate

The product 26 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (24.2 mg, 94% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J$ = 8.4 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 6.61 (d, $J$ = 15.9 Hz, 1H), 6.23 (dd, $J$ = 15.9, 8.0 Hz, 1H), 3.92 (s, 3H), 3.12 – 3.01 (m, 1H), 1.34 (d, $J$ = 7.0 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -72.38 (d, $J$ = 8.3 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.9, 140.8, 133.4, 130.1, 129.6, 127.1 (q, $J$ = 280.4 Hz), 127.0 (q, $J$ = 2.7 Hz), 126.5, 52.3, 42.1 (q, $J$ = 27.9 Hz), 13.7 (q, $J$ = 2.7 Hz). HRMS (EI): m/z calcd. for C$_{13}$H$_{13}$F$_3$O$_2$ [M]: 258.0868, found: 258.0867. [$\alpha$]$_D^{20}$ = 0.1 (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (2% isopropanol in hexanes, 0.5 mL/min, $\lambda$ = 254 nm), $t_R$ = 14.9 min (minor), 15.9 min (major), 90% ee.

methyl (E)-4-(3-(trifluoromethyl)non-1-en-1-yl)benzoate
The product 27 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (21.3 mg, 65% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \(J = 8.4\) Hz, 2H), 7.44 (d, \(J = 8.4\) Hz, 2H), 6.59 (d, \(J = 15.9\) Hz, 1H), 6.08 (dd, \(J = 15.9, 9.4\) Hz, 1H), 3.92 (s, 3H), 2.91 – 2.79 (m, 1H), 1.85 – 1.77 (m, 1H), 1.61 – 1.52 (m, 1H), 1.43 – 1.23 (m, 8H), 0.87 (t, \(J = 6.5\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.9, 140.8, 134.9, 130.1, 129.6, 127.0 (q, \(J = 281.0\) Hz), 126.5, 126.1 (q, \(J = 2.7\) Hz), 52.3, 48.1 (q, \(J = 26.5\) Hz), 31.7, 29.1, 28.0, 26.7, 22.7, 14.2. HRMS (ESI): m/z calcd. for C\(_{18}\)H\(_{24}\)F\(_3\)O\(_2\) + [M + H]: 329.1723, found: 329.1727. 

\[\text{[\(\alpha\)]}_{D}^{20} = 1.1\ (c = 1.0, \text{CHCl}_3),\ \text{HPLC chiralcel OD-H column (2\% iso-propanol in hexanes, 0.2 mL/min, } \lambda = 254\ \text{nm), } t_R = 21.4\ \text{min (major), 96\% ee.}\]

**methyl (E)-4-(3-(trifluoromethyl)tetradec-1-en-1-yl)benzoate**

The product 28 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (23.0 mg, 58% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \(J = 8.5\) Hz, 2H), 7.44 (d, \(J = 8.5\) Hz, 2H), 6.59 (d, \(J = 15.8\) Hz, 1H), 6.08 (dd, \(J = 15.9, 9.3\) Hz, 1H), 3.92 (s, 3H), 2.90 – 2.80 (m, 1H), 1.84 – 1.78 (m, 1H), 1.41 – 1.24 (m, 19H), 0.87 (t, \(J = 6.9\) Hz, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -70.64 (d, \(J = 8.7\) Hz). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 166.9, 140.8, 134.9, 130.1, 129.6, 127.0 (q, \(J = 280.4\) Hz), 126.5, 126.1 (q, \(J = 2.6\) Hz), 52.3, 48.1 (q, \(J = 26.7\) Hz), 32.0, 29.7, 29.7, 29.49, 29.47, 29.4, 28.0 (d, \(J = 2.1\) Hz), 26.7, 22.8, 14.3. HRMS (ESI): m/z calcd. for C\(_{23}\)H\(_{34}\)F\(_3\)O\(_2\) + [M + H]: 399.2505, found: 399.2506. \([\alpha]_D^{20} = 1.2\ (c = 1.0, \text{CHCl}_3),\ \text{HPLC chiralcel OD-H column (2\% iso-propanol in hexanes, 0.2 mL/min, } \lambda = 254\ \text{nm), } t_R = 20.9\ \text{min (minor), 95\% ee.}\]

**methyl (E)-4-(3-(cyclohexylmethyl)-4,4,4-trifluorobut-1-en-1-yl)benzoate**

The product 29 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (23.7 mg, 70% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \(J = 8.4\) Hz, 2H), 7.45 (d, \(J = 8.4\) Hz, 2H), 6.59 (d, \(J = 15.9\) Hz, 1H), 6.06 (dd, \(J = 15.9, 9.3\) Hz, 1H), 3.92 (s, 3H), 3.04 – 2.94 (m, 1H), 1.78 – 1.62 (m, 5H), 1.61 – 1.57 (m, 1H), 1.55 – 1.49 (m, 1H), 1.34 – 1.25 (m, 1H), 1.23 – 1.10 (m, 3H), 1.04 – 0.96 (m, 1H), 0.89 – 0.81 (m, 1H). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -70.71 (d, \(J = 9.0\) Hz). \(^{13}\)C NMR (126 MHz, CDCl\(_3\))
δ 166.9, 140.8, 134.7, 130.1, 129.5, 127.1 (q, J = 280.4 Hz), 126.5, 126.2 (q, J = 2.8 Hz), 52.3, 45.3 (q, J = 26.7 Hz), 35.3, 34.3, 34.1, 31.9, 26.5, 26.2, 26.0. HRMS (ESI): m/z calcd. for C_{19}H_{24}F_{3}O_{2}^+ [M + H^+] : 341.1723, found: 341.1731. [α]_D^{20} = 0.7 (c = 1.0, CHCl_3), HPLC chiralcel OD-H column (1% isopropanol in hexanes, 0.3 mL/min, λ = 254 nm), t_R = 16.1 min (minor), 17.0 min (major), 94% ee.

**methyl (E)-4-(7-chloro-3-(trifluoromethyl)hept-1-en-1-yl)benzoate**

The product 30 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (28.1 mg, 81% yield). ^1^H NMR (500 MHz, CDCl_3) δ 8.00 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 15.9, 9.4 Hz, 1H), 3.92 (s, 3H), 3.52 (t, J = 6.6 Hz, 2H), 2.91 – 2.81 (m, 1H), 1.87 – 1.74 (m, 3H), 1.63 – 1.55 (m, 1H), 1.54 – 1.39 (m, 3H), 1.36 – 1.28 (m, 1H). ^1^F NMR (471 MHz, CDCl_3) δ -70.63 (d, J = 8.8 Hz). ^1^C NMR (126 MHz, CDCl_3) δ 166.9, 140.6, 135.1, 130.1, 129.6, 126.9 (q, J = 280.2 Hz), 126.5, 125.6 (q, J = 2.7 Hz), 52.3, 48.0 (q, J = 26.6 Hz), 45.0, 32.4, 27.8, 26.6, 26.0. HRMS (EI): m/z calcd. for C_{17}H_{20}ClF_{3}O_{2}^+ [M]: 348.1104, found: 348.1098. [α]_D^{20} = 0.7 (c = 1.0, CHCl_3), HPLC chiralcel OD-H column (2% isopropanol in hexanes, 0.5 mL/min, λ = 254 nm), t_R = 14.3 min (minor), 20.9 min (major), 96% ee.

**methyl (E)-4-(5-(4-chlorophenyl)-3-(trifluoromethyl)pent-1-en-1-yl)benzoate**

The product 31 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (27.2 mg, 71% yield). ^1^H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9, 9.4 Hz, 1H), 3.93 (s, 3H), 2.91 – 2.82 (m, 1H), 2.79 – 2.72 (m, 1H), 2.61 – 2.53 (m, 1H), 2.20 – 2.11 (m, 1H), 1.94 – 1.85 (m, 1H) ^1^F NMR (376 MHz, CDCl_3) δ -70.49 (d, J = 8.5 Hz). ^1^C NMR (101 MHz, CDCl_3) δ 166.9, 140.5, 139.0, 135.7, 132.3, 130.2, 129.9, 129.8, 128.9, 126.8 (q, J = 280.6 Hz), 126.6, 125.2 (d, J = 2.6 Hz), 52.3, 47.3 (q, J = 26.8 Hz), 32.0, 29.3. HRMS (ESI): m/z calcd. for C_{20}H_{18}ClF_{3}O_{2}^+ [M + H^+] : 383.1020, found: 383.1030. [α]_D^{20} = 1.0 (c = 1.0, CHCl_3), HPLC chiralcel AS-H column (4% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), t_R = 8.2 min (major), 21.5 min (minor), 94% ee.
methyl (E)-4-(5-(4-methoxyphenyl)-3-(trifluoromethyl)pent-1-en-1-yl)benzoate

The product 32 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (32.1 mg, 85% yield). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.02 (d, \( J = 8.3 \) Hz, 2H), 7.46 (d, \( J = 8.3 \) Hz, 2H), 7.09 (d, \( J = 8.6 \) Hz, 2H), 6.84 (d, \( J = 8.6 \) Hz, 2H), 6.59 (d, \( J = 15.9 \) Hz, 1H), 6.12 (dd, \( J = 15.9, 9.4 \) Hz, 1H), 3.93 (s, 3H), 3.79 (s, 3H), 2.93 – 2.81 (m, 1H), 2.77 – 2.70 (m, 1H), 2.58 – 2.50 (m, 1H), 2.19 – 2.11 (m, 1H), 1.93 – 1.84 (m, 1H). \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -70.46 (d, \( J = 8.8 \) Hz). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.9, 158.2, 140.7, 135.5, 132.6, 130.1, 129.7, 129.5, 126.9 (q, \( J = 280.8 \) Hz), 126.5, 125.5 (q, \( J = 2.5 \) Hz), 114.1, 55.4, 52.3, 47.2 (q, \( J = 26.8 \) Hz), 31.6, 29.6. HRMS (ESI): m/z calcd. for C\(_{21}\)H\(_{22}\)F\(_3\)O\(_3\)\([M + H]^+\): 379.1516, found: 379.1517.

\( [\alpha]_D^{20} = 1.4 \) (c = 1.0, CHCl\(_3\)), HPLC chiralcel O-D column (5% isopropanol in hexanes, 0.5 mL/min, \( \lambda = 254 \) nm), \( t_R = 23.8 \) min (major), 26.4 min (minor), 94% ee.

methyl (E)-4-(6-(benzoyloxy)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate

The product 33 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (29.2 mg, 72% yield). \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.04 – 7.99 (m, 4H), 7.56 (t, \( J = 7.5 \) Hz, 1H), 7.46 – 7.43 (m, 4H), 6.64 (d, \( J = 15.9 \) Hz, 1H), 6.11 (dd, \( J = 15.9, 9.3 \) Hz, 1H), 4.35 (t, \( J = 6.2 \) Hz, 2H), 3.92 (s, 3H), 3.00 – 2.91 (m, 1H), 2.06 – 1.99 (m, 1H), 1.95 – 1.87 (m, 1H), 1.84 – 1.70 (m, 2H). \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -70.61 (d, \( J = 8.2 \) Hz). \( ^{13}C \) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 166.8, 166.6, 140.5, 135.6, 133.2, 130.3, 130.1, 129.8, 129.7, 128.6, 126.8 (q, \( J = 280.1 \) Hz), 126.6, 125.1 (d, \( J = 2.8 \) Hz), 64.2, 52.2, 47.8 (q, \( J = 27.1 \) Hz), 26.1, 24.8. HRMS (ESI): m/z calcd. for C\(_{22}\)H\(_{22}\)F\(_3\)NaO\(_4\)\([M + Na]^+\): 429.1284, found: 429.1283. \( [\alpha]_D^{20} = 0.4 \) (c = 1.0, CHCl\(_3\)), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, \( \lambda = 254 \) nm), \( t_R = 13.0 \) min (minor), 15.0 min (major), 94% ee.

tert-butyl (E)-4-(4-(4-(methoxycarbonyl)phenyl)-2-(trifluoromethyl)but-3-en-1-yl)piperidine-1-carboxylate

S30
The product 34 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (35.6 mg, 81% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.07 (dd, $J = 15.9, 9.3$ Hz, 1H), 4.13 – 4.07 (m, 2H), 3.92 (s, 3H), 3.05 – 2.93 (m, 1H), 2.70 – 2.58 (m, 2H), 1.71 – 1.56 (m, 5H), 1.44 (s, 9H), 1.28 – 1.02 (m, 2H).

$_{19}$F NMR (376 MHz, CDCl$_3$) δ -70.72 (d, $J = 8.7$ Hz).

$_{13}$C NMR (101 MHz, CDCl$_3$) δ 166.8, 154.9, 140.5, 135.1, 130.2, 129.8, 126.9 (q, $J = 280.9$ Hz), 126.6, 125.6 (q, $J = 25.4$ Hz), 79.6, 52.3, 45.2 (q, $J = 26.8$ Hz), 34.6, 33.0, 32.8, 31.0, 28.6. HRMS (ESI): m/z calcd. for C$_{23}$H$_{30}$F$_3$NNaO$_4$+: [M + Na$^+$]: 464.2019, found: 464.2025.

$[^{[\alpha]}]_D^{20} = 1.7$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 16.9$ min (major), 18.9 min (minor), 96% ee.

(E)-6-(4-(methoxycarbonyl)phenyl)-4-(trifluoromethyl)hex-5-en-1-yl furan-2-carboxylate

The product 35 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (32.8 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.58 (dd, $J = 1.8, 0.9$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.18 (dd, $J = 3.5, 0.9$ Hz, 1H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.51 (dd, $J = 3.5, 1.7$ Hz, 1H), 6.09 (dd, $J = 15.9, 9.3$ Hz, 1H), 4.33 (t, $J = 6.2$ Hz, 2H), 3.91 (s, 3H), 3.01 – 2.89 (m, 1H), 2.12 – 1.65 (m, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.64 (d, $J = 8.9$ Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.9, 158.8, 146.6, 144.6, 140.4, 135.6, 130.1, 129.7, 126.7 (q, $J = 280.5$ Hz), 126.6, 125.0, 118.2, 112.0, 64.3, 52.3, 47.8 (q, $J = 27.1$ Hz), 26.0, 24.6. HRMS (ESI): m/z calcd. for C$_{23}$H$_{30}$F$_3$NNaO$_4$+: [M + Na$^+$]: 419.1077, found: 419.1083. $[^{[\alpha]}]_D^{20} = 0.8$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 16.1$ min (minor), 19.4 min (major), 95% ee.

methyl (E)-4-(6-(1,3-dioxoisoadolin-2-yl)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate

The product 36 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (34.0 mg,
79% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, $J = 6.7$ Hz, 2H), 7.91 – 7.76 (m, 2H), 7.71 – 7.69 (m, 2H), 7.42 (d, $J = 6.6$ Hz, 2H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.06 (dd, $J = 15.8$, 9.4 Hz, 1H), 3.90 (s, 3H), 3.71 (t, $J = 6.2$ Hz, 2H), 2.99 – 2.90 (m, 1H), 1.89 – 1.60 (m, 4H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.60 (d, $J = 8.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 168.4, 166.8, 140.4, 135.6, 134.2, 132.1, 130.1, 129.6, 126.7 (q, $J = 280.2$ Hz), 126.6, 125.0 (q, $J = 2.8$ Hz), 123.4, 52.2, 47.7 (q, $J = 26.9$ Hz), 37.4, 25.8, 25.2.

HRMS (ESI): m/z calcd. for C$_{23}$H$_{21}$F$_3$NO$_4$ $^{[M + H]^+}$: 432.1417, found: 432.1432.

[α]$_D^{20}$ = 3.2 (c = 2.0, CHCl$_3$), HPLC chiralcel OD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R$ = 15.5 min (minor), 24.8 min (major), 92% ee.

**methyl (E)-4-(4,4,5,5,5-pentafluoro-3-phenylpent-1-en-1-yl)benzoate**

The product 38 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (34.3 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.31 (dd, $J = 8.0$, 6.7 Hz, 2H), 7.25 – 7.14 (m, 3H), 6.56 (d, $J = 15.8$ Hz, 1H), 6.09 (dd, $J = 15.9$, 9.8 Hz, 1H), 3.93 (s, 3H), 3.97 – 2.77 (m, 2H), 2.60 – 2.53 (m, 1H), 2.60 – 2.21 (m, 1H), 1.96 – 1.87 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.47 (s), -116.30 (dd, $J = 269.6$, 9.4 Hz), -122.11 (dd, $J = 269.9$, 20.4 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.9, 140.6, 135.4, 130.2, 129.8, 128.7, 128.5, 126.6, 126.5, 125.1.
HRMS (ESI): m/z calcd. for C_{21}H_{20}F_{5}O_{2}^{+} [M + H^{+}]: 399.1378, found: 399.1384. [α]_{D}^{20} = 0.7 (c = 1.0, CHCl_{3}), HPLC chiralcel OD-H column (2% isopropanol in hexanes, 0.5 mL/min, λ = 254 nm), t_{R} = 29.6 min (minor), 31.0 min (major), 96% ee.

(E)-7-phenyl-5-(trifluoromethyl)hept-3-en-1-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate

The product 39 was purified with silica gel chromatography (PE/EA = 20/1) as a colorless oil (29.0 mg, 60% yield). ^{1}H NMR (500 MHz, CDCl_{3}) δ 7.54 – 7.51 (m, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.15 – 7.11 (m, 4H), 5.61 (dt, J = 14.4, 6.8 Hz, 1H), 5.36 (dt, J = 15.6, 8.4 Hz, 1H), 4.25 – 4.13 (m, 2H), 3.75 (q, J = 7.1 Hz, 1H), 2.74 – 2.60 (m, 2H), 2.52 – 2.41 (m, 3H), 2.08 – 2.01 (m, 1H), 1.79 – 1.69 (m, 1H), 1.54 (dd, J = 7.2, 3.3 Hz, 3H). ^{1}F NMR (471 MHz, CDCl_{3}) δ -70.99 (d, J = 8.7 Hz), -117.29 – -117.85 (m). ^{13}C NMR (126 MHz, CDCl_{3}) δ 174.1, 159.8 (d, J = 248.3 Hz), 141.9 (d, J = 7.5 Hz), 140.8, 135.6, 133.1, 130.9 (d, J = 4.2 Hz), 129.1 (d, J = 3.2 Hz), 128.7, 128.6, 128.5, 128.0 (d, J = 13.5 Hz), 127.8, 127.0 (q, J = 280.1 Hz), 126.4, 126.2, 123.7, 115.4 (d, J = 23.8 Hz), 63.9 (d, J = 3.8 Hz), 46.9 (q, J = 26.7 Hz), 45.2, 32.5, 32.0, 29.2, 18.5. HRMS (ESI): m/z calcd. for C_{29}H_{28}F_{4}NaO_{2}^{+} [M + Na^{+}]: 507.1918, found: 507.1922. [α]_{D}^{20} = 0.3 (c = 1.0, CHCl_{3}), HPLC chiralcel AS-H column contacted with another AS-H column (1.5% isopropanol in hexanes, 0.3 mL/min, λ = 254 nm), t_{R} = 36.2 min (major), 38.2 min (minor), 42.6 min (major), 51.1 min (minor), 93% ee, dr = 1:1.

(E)-7-phenyl-5-(trifluoromethyl)hept-3-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

The product 40 was purified with silica gel chromatography (PE/EA = 3/1) as a yellow oil (39.5 mg, 66% yield). ^{1}H NMR (500 MHz, CDCl_{3}) δ 7.65 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.15 (d, J = 7.5 Hz, 2H), 6.97 (s, 1H), 6.87 (d, J = 9.0 Hz, 1H), 6.68 (d, J = 9.2 Hz, 1H), 5.61 (dt, J = 14.4, 6.9 Hz, 1H), 5.37 (dd, J = 15.5, 9.1 Hz, 1H), 4.23 – 4.15 (m, 2H), 3.83
(s, 3H), 3.67 (s, 2H), 2.73 – 2.59 (m, 2H), 2.38 (s, 3H), 2.08 – 2.01 (m, 1H), 1.78 – 1.70 (m, 1H). 19F NMR (471 MHz, CDCl3) δ -70.96 (d, J = 8.8 Hz). 13C NMR (126 MHz, CDCl3) δ 170.9, 168.4, 156.2, 140.8, 139.4, 136.1, 134.0, 133.0, 131.3, 130.9, 130.8, 129.2, 128.7, 128.5, 127.0 (q, J = 280.1 Hz), 126.4, 126.3 (q, J = 2.7 Hz), 115.1, 112.6, 111.6, 101.5, 64.0, 55.8, 46.9 (q, J = 26.5 Hz), 32.4, 32.1, 30.4, 29.1, 13.4. HRMS (ESI): m/z calcd. for C33H32ClF3NO4+: [M + H]+: 598.1966, found: 598.1976. [α]D20 = 0.3 (c = 1.0, CHCl3), HPLC chiralcel OD-H column (5% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm), tR = 35.9 min (major), 44.0 min (minor), 86% ee.

(E)-7-phenyl-5-(trifluoromethyl)hept-3-en-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate

The product 41 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (31.3 mg, 56% yield). 1H NMR (500 MHz, CDCl3) δ 7.71 (dd, J = 19.3, 6.7 Hz, 4H), 7.44 (d, J = 6.5 Hz, 2H), 7.29 (t, J = 7.1 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.14 (d, J = 7.4 Hz, 2H), 6.85 (d, J = 6.7 Hz, 2H), 5.55 (dt, J = 14.6, 6.7 Hz, 1H), 5.33 (dd, J = 15.5, 9.1 Hz, 1H), 4.29 – 4.20 (m, 2H), 2.73 – 2.57 (m, 2H), 2.51 – 2.39 (m, 3H), 2.07 – 2.00 (m, 1H), 1.75 – 1.67 (m, 7H). 19F NMR (471 MHz, CDCl3) δ -70.95 (d, J = 8.7 Hz). 13C NMR (126 MHz, CDCl3) δ 194.3, 173.8, 159.7, 140.8, 138.5, 136.5, 132.7, 132.2, 131.3, 130.5, 128.7, 128.5, 126.9 (q, J = 280.1 Hz), 126.43 (q, J = 2.6 Hz), 126.37, 117.4, 79.5, 64.6, 46.9 (q, J = 26.7 Hz), 32.5, 31.9, 29.2, 25.5. HRMS (ESI): m/z calcd. for C31H31ClF3O4+ [M + H]+: 559.1857, found: 559.1859. [α]D20 = 0.3 (c = 1.0, CHCl3), HPLC chiralcel AD-H column (2% isopropanol in hexanes, 0.5 mL/min, λ = 254 nm), tR = 43.1 min (major), 45.6 min (minor), 94% ee.

Methyl 4-(((E)-6-(((tert-butoxycarbonyl)-L-phenylalanyl)oxy)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate

The product 42 was purified with silica gel chromatography (PE/EA = 5/1) as a colorless oil (30.1 mg, 55% yield). 1H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.28 – 7.18 (m, 3H), 7.13 – 7.11 (m, 2H), 6.60 (d, J = 15.9 Hz, 1H), 6.05 (dd, J = 15.9, 9.3 Hz, 1H), 4.97 – 4.95 (m, 1H), 4.58 – 4.53 (m, 1H), 4.15 – 4.02 (m, 2H), 3.92 (s, 3H), 3.05 (d, J = 6.4 Hz, 2H), 2.88 – 2.81 (m,
1H), 1.83 – 1.76 (m, 1H), 1.73 – 1.61 (m, 1H), 1.58 – 1.48 (m, 2H), 1.41 (s, 9H). $^1$H NMR (376 MHz, CDCl$_3$) $\delta$ -70.58 (d, $J = 8.7$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.2, 166.9, 155.2, 140.4, 136.1, 135.6, 130.2, 129.8, 129.4, 128.7, 127.2, 126.7 (q, $J = 281.1$ Hz), 126.6, 125.1, 80.2, 64.6, 54.7, 52.3, 47.8 (q, $J = 27.2$ Hz), 38.7, 28.4, 25.8, 24.6. HRMS (ESI): m/z calcd. for $C_{25}H_{33}F_3NO_6$: [M + H$^+$]: 550.2411, found: 550.2416. 

$[^\alpha]_D^{20}$ = 0.2 (c = 1.0, CHCl$_3$), HPLC chiralcel AS-H column (2% isopropanol in hexanes, 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ = 85.1 min (major), 115.8 min (minor), 94% $de$. 

methyl 4-(((E)-6-((S)-2-(4-isobutylphenyl)propanoyl)oxy)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate

The product 43 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (35.7 mg, 73% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.1$ Hz, 2H), 6.54 (d, $J = 15.9$ Hz, 1H), 5.99 (dd, $J = 15.9$, 9.4 Hz, 1H), 4.14 – 4.03 (m, 2H), 3.92 (s, 3H), 3.69 (q, $J = 7.2$ Hz, 1H), 2.86 – 2.75 (m, 1H), 2.42 (d, $J = 7.2$ Hz, 2H), 1.86 – 1.76 (m, 2H), 1.73 – 1.65 (m, 1H), 1.60 – 1.47 (m, 5H), 0.88 (d, $J = 6.6$ Hz, 6H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.69 (d, $J = 8.6$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.9, 166.9, 140.8, 140.5, 137.8, 135.4, 130.1, 129.7, 129.5, 127.2, 126.7 (q, $J = 280.7$ Hz), 126.5, 125.2 (q, $J = 2.8$ Hz), 63.8, 52.3, 47.6 (q, $J = 27.0$ Hz), 45.3, 45.1, 30.3, 25.8, 24.4, 22.5, 18.5. HRMS (ESI): m/z calcd. for $C_{28}H_{33}F_3NaO_4$: [M + Na$^+$]: 513.2223, found: 513.2226. $[^\alpha]_D^{20}$ = 0.6 (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ = 7.1 min (major), 7.9 min (minor), 96% $de$. 

methyl 4-(((E)-6-((S)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate

The product 44 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (34.8 mg, 68% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.68 (t, $J = 8.3$ Hz, 3H), 7.39 (dd, $J = 8.4$, 1.8 Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.19 – 7.02 (m, 2H), 6.45 (d, $J = 15.9$ Hz, 1H), 5.90 (dd, $J = 15.8$, 9.3 Hz, 1H), 4.17 – 4.05 (m, 2H), 3.92 – 3.82 (m, 7H), 2.84 – 2.74 (m, 1H), 1.81 – 1.75 (m, 1H), 1.72 – 1.65 (m, 1H), 1.60 – 1.44 (m, 5H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.66 (d, $J = 8.8$ Hz). $^{13}$C
NMR (151 MHz, CDCl$_3$) $\delta$ 174.8, 166.9, 157.8, 140.4, 135.7, 135.4, 133.8, 130.1, 129.6, 129.4, 129.0, 127.3, 126.6 (q, $J = 280.3$ Hz), 126.5, 126.3, 126.1, 125.1, 119.2, 105.6, 64.0, 55.4, 52.3, 47.6 (q, $J = 27.1$ Hz), 45.6, 25.8, 24.5, 18.5. HRMS (ESI): m/z calcd. for C$_{29}$H$_{30}$F$_3$O$_5$ $\left[\text{M} + \text{H}^+\right]$: 515.2040, found: 515.2047. $[\alpha]_D^{19} = 1.4$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 19.6$ min (major), 22.2 min (minor), 94% de.

**methyl (E)-4-(6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate**

The product 45 was purified with silica gel chromatography (PE/EA = 10/1) as a colorless oil (37.4 mg, 70% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.79 – 6.52 (m, 3H), 6.08 (dd, $J = 15.9$, 9.3 Hz, 1H), 4.09 (t, $J = 6.1$ Hz, 2H), 3.92 (s, 3H), 3.91 – 3.89 (m, 2H), 2.93 – 2.86 (m, 1H), 2.30 (s, 3H), 1.96 – 1.89 (m, 1H), 1.82 – 1.72 (m, 5H), 1.67 – 1.62 (m, 2H), 1.22 (s, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.68 (d, $J = 9.2$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.9, 166.8, 157.0, 140.4, 136.6, 135.5, 130.4, 130.1, 129.8, 126.7 (q, $J = 280.0$ Hz), 126.6, 125.1, 123.7, 120.9, 112.1, 68.0, 63.6, 52.3, 47.7 (q, $J = 26.7$ Hz), 42.3, 37.2, 25.9, 25.33, 25.30, 24.6, 21.5, 15.9. HRMS (ESI): m/z calcd. for C$_{30}$H$_{37}$F$_3$NaO$_5$ $\left[\text{M} + \text{Na}^+\right]$: 557.2485, found: 557.2491. $[\alpha]_D^{19}$ = 1.0 (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (3% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 12.9$ min (major), 14.0 min (minor), 95% ee.

**methyl (E)-4-(6-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-8-yl)acetoxy)-3-(trifluoromethyl)hex-1-en-1-yl)benzoate**

The product 46 was purified with silica gel chromatography (PE/EA = 5/1) as a colorless oil (47.3 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 2.4$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.87 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.48 – 7.39 (m, 4H), 7.35 (d, $J = 7.4$ Hz, 1H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.05 (dd, $J = 15.9$, 9.3 Hz, 1H), 5.15 (s, 2H), 4.13 (t, $J = 6.0$ Hz, 2H), 3.91 (s, 3H), 3.64 (s, 2H), 2.90 – 2.81 (m, 1H), 1.93 – 1.55 (m, 5H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.59 (d, $J = 8.3$ Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 190.9, 171.5, 166.8, 160.6, 140.5, 140.4, 136.4, 135.6, 135.5, 132.9, 132.5,
130.1, 129.7 (q, $J = 280.2$ Hz), 129.6, 129.4, 127.9, 127.8, 126.7, 126.6, 125.2, 125.1, 121.2, 73.7, 64.3, 52.3, 47.7 (q, $J = 26.7$ Hz), 40.4, 25.8, 24.6. HRMS (ESI): m/z calcd. for C$_{31}$H$_{27}$F$_3$NaO$_5$ $^+$ [M + Na$^+$]: 575.1652, found: 575.1658. $[^\alpha]_D^{20} = 1.2$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (40% isopropanol in hexanes, 0.5 mL/min, $\lambda = 254$ nm), $t_R = 30.7$ min (minor), 34.2 min (major), 96% ee.

$^{(E)}$-6-(4-(methoxycarbonyl)phenyl)-4-(trifluoromethyl)hex-5-en-1-yl $^2$-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate

The product 47 was purified with silica gel chromatography (PE/EA = 5/1) as a white solid (31.4 mg, 52% yield); mp: 95-97 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 2.3$ Hz, 1H), 8.07 (dd, $J = 8.9$, 2.3 Hz, 1H), 8.00 (d, $J = 8.5$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.9$ Hz, 1H), 6.65 (d, $J = 15.9$ Hz, 1H), 6.11 (dd, $J = 15.9$, 9.3 Hz, 1H), 4.32 (t, $J = 6.1$ Hz, 2H), 4.03 – 3.77 (m, 5H), 3.04 – 2.89 (m, 1H), 2.75 (s, 3H), 2.24 – 2.16 (m, 1H), 2.03 – 1.97 (m, 1H), 1.93 – 1.86 (m, 1H), 1.84 – 1.69 (m, 2H), 1.09 (d, $J = 6.7$ Hz, 6H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.60 (d, $J = 8.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.5, 166.8, 162.7, 162.1, 161.7, 140.4, 135.7, 132.7, 132.3, 130.2, 129.8, 126.7 (q, $J = 280.5$ Hz), 126.6, 126.1, 125.1, 121.5, 115.5, 112.8, 103.2, 75.9, 64.6, 52.3, 47.8 (q, $J = 26.7$ Hz), 29.8, 28.3, 26.0, 24.7, 19.2, 17.6. HRMS (ESI): m/z calcd. for C$_{31}$H$_{27}$F$_3$NaO$_5$ $^+$ [M + H$^+$]: 601.1979, found: 601.1982. $[^\alpha]_D^{20} = 0.3$ (c = 1.0, CHCl$_3$), HPLC chiralcel AD-H column (10% isopropanol in hexanes, 1.0 mL/min, $\lambda = 254$ nm), $t_R = 48.5$ min (minor), 60.5 min (major), 95% ee.

$^{(E)}$-6-(4-(methoxycarbonyl)phenyl)-4-(trifluoromethyl)hex-5-en-1-yl $^2$-((E)-3-(3,4-dimethoxyphenyl)acrylamido)benzoate

The product 48 was purified with silica gel chromatography (PE/EA = 5/1) as a white solid (44.6 mg, 73% yield); mp: 134-136 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 11.24 (s, 1H), 8.88 (dd, $J = 8.5$, 1.2 Hz, 1H), 8.04 – 7.98 (m, 3H), 7.69 (d, $J = 15.4$ Hz, 1H), 7.60 – 7.56 (m, 1H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.15 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.87 (d, $J = 8.3$ Hz, 1H), 6.64 (d, $J = 15.8$ Hz, 1H), 6.46 (d, $J = 15.5$ Hz, 1H), 6.11 (dd, $J = 15.9$, 9.3 Hz, 1H), 4.38 (t, $J = 6.2$ Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 2.99 – 2.92 (m, 1H), 2.07 – 2.00 (m, 1H), 1.99 – 1.91 (m, 1H), 1.87 – 1.72 (m, 2H). $^{19}$F NMR (471
MHz, CDCl$_3$) $\delta$ -70.56 (d, $J = 8.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.6, 166.8, 164.9, 151.1, 149.4, 142.5, 142.3, 140.3, 135.7, 135.0, 130.8, 130.1, 129.9, 127.8, 126.7 (q, $J = 279.6$ Hz), 126.6, 125.0, 122.7, 122.6, 120.8, 119.7, 114.8, 111.2, 109.9, 64.7, 56.12, 56.09, 52.3, 47.8 (q, $J = 27.3$ Hz), 26.0, 24.8. HRMS (ESI): m/z calcd. for C$_n$H$_m$F$_n$NO$_n$ $^{[M+H]^+}$: 612.2204, found: 612.2209. $[\alpha]_D^{20} = 1.2$ (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (50% isopropanol in hexanes, 0.5 mL/min, $\lambda = 254$ nm), $t_R = 21.9$ min (minor), 41.5 min (major), 95% ee.

**Unsuccessful substrates**

![Unsuccessful substrates](chart)

Among these unsuccessful substrates, S7-S11 only gave trace amount of coupling products while S12 failed to proceed the coupling reaction with starting material remained.
Synthetic Utility

1 mmol scale reaction

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{Br} \quad \text{Ph} \\
1\text{a} & \quad \text{CF}_2 \\
\text{MeO}_2\text{C} & \quad \text{Br} \quad \text{Ph} \\
2\text{a} & \quad \text{CF}_2 \\
\text{NiBr}_2\cdot\text{DME} & \quad (10 \text{ mol\%}) \\
\text{L9} & \quad (13 \text{ mol\%}) \\
\text{Mn} & \quad (2.0 \text{ equiv}) \\
\text{THF}:\text{N,N-Dimethylpropionamide} & \quad = 9:1 (0.2 \text{ M}) \\
\text{TBAI} & \quad (1.0 \text{ equiv}) \\
\hline
\text{MeO}_2\text{C} & \quad \text{Br} \quad \text{Ph} \\
3 & \quad \text{CF}_2 \\
\text{-4}^\circ\text{C}, 40 \text{ h} \\
\text{NiBr}_2\cdot\text{DME} (10 \text{ mol\%}, 0.1 \text{ mmol, 31 mg}), \text{L9} (13 \text{ mol\%}, 0.13 \text{ mmol, 87 mg}), \text{Mn powder (2.0 equiv, 2.0 mmol, 110 mg), TBAI (1.0 equiv, 1.0 mmol, 369 mg) and vinyl iodide 1a (1.0 equiv, 1.0 mmol, 288 mg) were firstly combined in a 25 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N}_2 \text{ (repeated for 3 times). Alkyl bromide 2a (2.0 equiv, 2.0 mmol, 532 mg), THF (4.5 mL) and N,N-Dimethylpropionamide (0.5 mL) were added via syringe. The tube was sealed with a Teflon lined cap and stirred at -4 \text{ °C for 40 h. The reaction mixture was then diluted with ethyl acetate (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with ethyl acetate (3 × 15 mL), the combined organic layer was dried over Na}_2\text{SO}_4 \text{, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give coupling product 3 in 79% yield (275 mg) with 95% ee.}
\end{align*}
\]

Synthesis of diverse trifluoromethylated chiral analogues

Preparation of chiral trifluoromethylated alkane

The chiral $\alpha$-CF$_3$-substituted olefin 3 (34.8 mg, 0.1 mmol, 1.0 equiv.), Pd/C (5 mg) was added to a 25 mL oven-dried sealing tube. After that, the system was evacuated and a hydrogen-filled balloon was attached. The reaction was stirred at room temperature for 12 hours. The reaction mixture was then passed through a short pad of silica gel, with ethyl acetate as the eluent (~35 mL). The resulting mixture was concentrated, and the residue was purified by chromatography on silica gel to give the desired product 49.

**methyl (S)-4-(5-phenyl-3-(trifluoromethyl)pentyl)benzoate**
The product 49 was purified with silica gel chromatography (PE/EA = 30/1) as a colorless oil (32.6 mg, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 8.0$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.29 – 7.26 (m, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.18 (m, 2H), 3.95 (s, 3H), 2.79 – 2.71 (m, 4H), 2.18 – 1.97 (m, 3H), 1.88 – 1.78 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -69.59 (d, $J = 9.2$ Hz).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.1, 146.7, 141.1, 130.0, 128.7, 128.62 (q, $J = 281.0$ Hz), 128.55, 128.5, 128.4, 126.4, 52.2, 41.3 (q, $J = 24.9$ Hz), 33.0, 29.8, 29.5. HRMS (ESI): m/z calcd. for C$_{20}$H$_{21}$F$_3$NaO$_2$ $^+$ [M + Na$^+$]: 373.1386, found: 373.1388. 

[α]$_D^{20}$ = 0.2 (c = 1.0, CHCl$_3$), HPLC chiralcel OD-H column (2% isopropanol in hexanes, 1.0 mL/min, $\lambda = 214$ nm), $t_R$ = 24.9 min (minor), 28.0 min (major), 95% ee.

**Preparation of chiral trifluoromethylated styrene oxide derivatives**

To a test tube, the chiral $\alpha$-CF$_3$-substituted olefin 3 (34.8 mg, 0.1 mmol, 1.0 equiv.) and m-CPBA (138.1 mg, 0.8 mmol, 8.0 equiv.) in 1.5 mL of dichloromethane were stirred for 5 days at room temperature. After completion, the residue was purified by chromatography on silica gel to give the desired product 50.

**methyl 4-(3-((S)-1,1,1-trifluoro-4-phenylbutan-2-yl)oxiran-2-yl)benzoate**

The product 50 was purified with silica gel chromatography (PE/EA = 20/1) as a colorless oil (23.1 mg, 63% yield), $dr = 2:1$. **50-major:** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 2H), 7.36–7.31 (m, 4H), 7.28 – 7.25 (m, 2H), 7.24 – 7.22 (m, 1H), 3.92 (s, 3H), 3.84 (d, $J = 1.9$ Hz, 1H), 3.01 – 2.93 (m, 2H), 2.90 – 2.84 (m, 1H), 2.22 – 2.02 (m, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -68.69 (d, $J = 8.4$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.8, 141.3, 140.7, 130.4, 130.0, 128.7, 128.6, 126.7 (q, $J = 280.9$ Hz), 126.5, 125.5, 60.7 (q, $J = 3.6$ Hz), 57.1, 52.3, 46.4 (q, $J = 25.5$ Hz), 32.6, 28.9. [α]$_D^{20}$ = 0.6 (c = 1.6, CHCl$_3$), HPLC chiralcel OD-H column (5% isopropanol in hexanes, 1.0 mL/min, $\lambda = 277$ nm), $t_R$ = 9.8 min (minor), 16.8 min (major), 95% ee. **50-minor:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 2H), 7.35 – 7.30 (m, 4H), 7.25 – 7.21 (m, 1H), 7.20 – 7.17 (m, 2H), 3.93 (s, 3H), 3.65 (d, $J = 2.0$ Hz, 3H), 3.62 (d, $J = 1.6$ Hz, 3H).
1H), 3.05 (dd, J = 7.9, 2.0 Hz, 1H), 2.85 – 2.71 (m, 2H), 2.25 – 2.05 (m, 2H), 1.94 – 1.84 (m, 1H). 19F NMR (471 MHz, CDCl3) δ -69.35 (d, J = 8.6 Hz). 13C NMR (126 MHz, CDCl3) δ 166.8, 141.3, 140.2, 130.6, 130.1, 128.9, 128.4, 127.1 (q, J = 281.7 Hz), 126.8, 125.6, 59.8, 56.1, 52.4, 45.6 (q, J = 25.7 Hz), 33.2, 26.7. [α]D20 = 0.9 (c = 0.8, CHCl3), HPLC chiralcel OD-H column (10% isopropanol in hexanes, 1.0 mL/min, λ = 240 nm), tR = 10.4 min (minor), 16.1 min (major), 95% ee. HRMS (ESI): m/z calcd. for C20H20F3O3+: M + H+: 365.1359, found: 365.1373.

**Preparation of chiral trifluoromethylated dihydroxylated alkane**

To a solution of the chiral α-CF3-substituted olefin 3 (34.8 mg, 0.1 mmol, 1.0 equiv.) in acetone (0.4 mL) and water (0.1 mL) was added OsO4 (32 µL, 5.0 mol %, 4.0 wt% in H2O) and then N-methylmorpholineN-oxide (17.6 mg, 0.15 mmol, 1.5 equiv). The mixture was stirred for 24 h at room temperature and then quenched by the addition of an aqueous saturated solution of Na2SO3 (5.0 mL). The organic phase was extracted with ethyl acetate (3 × 20 mL), the combined organic phases were washed with brine, dried over Na2SO4, and concentrated in vacuo. The residue was purified by chromatography on silica gel to give the desired product 51.

**methyl 4-((3S)-1,2-dihydroxy-5-phenyl-3-(trifluoromethyl)penty)benzoate**

The product 51 was purified with silica gel chromatography (PE/EA = 3/1) as a colorless oil (27.5 mg, 72% yield), dr = 2:1. 1H NMR (500 MHz, CDCl3) δ 7.99 (d, J = 8.4 Hz, 4H), 7.88 (d, J = 8.4 Hz, 2H), 7.36 – 7.28 (m, 7H), 7.21 – 7.13 (m, 8H), 6.98 – 6.96 (m, 6H), 4.88 (d, J = 6.6 Hz, 2H), 4.44 (d, J = 7.9 Hz, 1H), 4.03 (d, J = 8.0 Hz, 1H), 3.93 (s, 6H), 3.91 – 3.88 (m, J = 13.1 Hz, 5H), 3.02 – 2.82 (m, 7H), 2.70 – 2.59 (m, 3H), 2.53 – 2.47 (m, 2H), 2.14 – 1.93 (m, 9H). 19F NMR (471 MHz, CDCl3) δ -67.87 (d, J = 10.0 Hz), -65.78 (d, J = 10.0 Hz). 13C NMR (126 MHz, CDCl3) δ 166.84, 166.80, 145.4, 144.5, 141.0, 140.2, 130.2, 130.10, 130.05, 130.0, 128.84, 128.82, 128.6, 128.3, 128.0 (q, J = 281.7 Hz), 127.6 (q, J = 282.1 Hz), 127.0, 126.8, 126.5, 126.3, 74.6, 74.5, 74.3, 73.0, 52.31, 52.28, 43.0 (q, J = 24.0 Hz), 42.3 (q, J = 24.0 Hz), 33.5, 32.8, 27.6, 25.2. HRMS (ESI): m/z calcd. for C20H21F3NaO4+: [M + Na]+: 405.1284, found: 405.1290. [α]D20 = -0.2 (c = 1.0, CHCl3), HPLC chiralcel AY-H column contacted with another OD-H column (20% isopropanol in hexanes, 0.5 mL/min, λ = 254 nm), tR = 27.1 min (major), 29.7 min.
Preparation of chiral β-trifluoromethylated alcohol

To a solution of chiral α-CF₃-substituted olefin 3 (34.8 mg, 0.1 mmol, 1.0 equiv.) in CH₃CN (0.2 mL) was added CCl₄ (0.2 mL), H₂O (0.3 mL), and NaIO₄ (88.5 mg, 0.41 mmol, 4.1 equiv.). The biphasic mixture was vigorously stirred, and 5 mg of RuCl₃·H₂O was added in one portion. After 60 min the mixture was passed through a short pad of silica gel, with dichloromethane as the eluent (~60 mL). The combined organic layers were treated with Na₂SO₄ and concentrated under reduced pressure to afford the crude acid which was used directly.

To a solution of crude trifluoromethylated acid in THF (2 mL) was added LiAlH₄ (32 mg, 0.8 mmol, 8.0 equiv.) at -20 °C. Then, the mixture was stirred at room temperature for 4 h. After that, 1N HCl solution was added to quench the reaction. The organic phase was extracted with ethyl acetate (3 × 20 mL), the combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatography on silica gel to give the desired product 52.

(S)-4-phenyl-2-(trifluoromethyl)butan-1-ol

The product 52 was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (12.2 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.29 (m, 2H), 7.23 – 7.20 (m, 3H), 3.89 – 3.81 (m, 2H), 2.85 – 2.69 (m, 2H), 2.32 – 2.20 (m, 1H), 2.02 – 1.88 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -68.89 (d, J = 9.5 Hz). ¹³C NMR (126 MHz, CDCl₃) δ 141.0, 128.7, 128.5, 128.0 (q, J = 281.0 Hz), 126.4, 59.9 (q, J = 2.9 Hz), 44.8 (q, J = 24.2 Hz), 32.9, 26.4. HRMS (EI): m/z calcd. for C₁₁H₁₃F₃O [M]: 218.0918, found: 218.0909. [α]D₂₀ = 0.4 (c = 0.5, CHCl₃), HPLC chiralcel AD-H column (2% isopropanol in hexanes, 1.0 mL/min, λ = 214 nm), tₘₐᵢᵢᵣ = 14.9 min (minor), 15.8 min (major), 94% ee.

Preparation of chiral trifluoromethylated allyl alcohol
To a solution of chiral α-CF₃-substituted olefin 22 (14.3 mg, 0.05 mmol, 1.0 equiv.) in THF (1 mL) was added LiAlH₄ (4 mg, 0.1 mmol, 2.0 equiv.) at 0 °C. Then, the mixture was stirred at room temperature for 4 h. After that, 1N HCl solution was added to quench the reaction. The organic phase was extracted with ethyl acetate (3 × 20 mL), the combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatography on silica gel to give the desired product 53.

\[(S,E)-6\text{-phenyl-4-(trifluoromethyl)hex-2-en-1-ol}\]

The product 53 was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (8.3 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.28 (m, 2H), 7.24 – 7.16 (m, 3H), 5.86 (dt, J = 15.5, 5.1 Hz, 1H), 5.60 – 5.53 (m, 1H), 4.20 (dd, J = 5.1, 1.7 Hz, 2H), 2.79 – 2.67 (m, 2H), 2.60 – 2.52 (m, 1H), 2.13 – 2.05 (m, 1H), 1.86 – 1.76 (m, 1H), 1.65 – 1.56 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -70.87 (d, J = 9.6 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 136.3, 128.7, 128.6, 126.9 (q, J = 280.7 Hz), 126.4, 124.4 (q, J = 2.5 Hz), 63.0, 46.6 (q, J = 26.5 Hz), 32.6, 29.3. HRMS (EI): m/z calcd. for C₁₃H₁₅F₃O [M]: 244.1075, found: 244.1076. [α]D²⁰ = 0.5 (c = 0.25, CHCl₃), HPLC chiralecel AD-H column (1% isopropanol in hexanes, 1.0 mL/min, λ = 214 nm), tᵣ = 27.4 min (minor), 30.5 min (major), 97% ee.

**Preparation of chiral trifluoromethylated ketone**

CuI (4.0 mg, 0.021 mmol, 0.3 equiv.) was firstly added to a 10 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N₂ (repeated for 3 times). 0.1 mL of tert-Butyl methyl ether was added to the system and the tube was transferred to -50 °C. Then, PhMgBr solution (0.35 mL, 1M in THF, 5.0 equiv.) was added under N₂ atmosphere. After stirring at this temperature for 10 min, chiral α-CF₃-substituted olefin 22 (20.0 mg, 0.07 mmol, 1.0 equiv.) in tert-Butyl methyl ether (0.2 mL) was added dropwise. The reaction was stirred at -50 °C for additional 8 h. After that, MeOH (0.5 mL) and sat. NH₄Cl solution (1.0 mL) was added to quench the reaction. The organic phase was extracted with ethyl acetate (3 × 20 mL), the combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatography on silica gel to give the desired product 54.
(4S)-1,3,6-triphenyl-4-(trifluoromethyl)hexan-1-one

The product 54 was purified with silica gel chromatography (PE/EA = 30:1) as a colorless oil (22.5 mg, 81% yield), $dr = 20:1$ according to the $^{19}$F NMR. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 – 7.91 (m, 2H), 7.59 – 7.54 (m, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.16 (m, 6H), 7.06 – 7.04 (m, 2H), 4.04 – 3.99 (m, 1H), 3.65 (dd, $J = 17.7$, 9.6 Hz, 1H), 3.40 (dd, $J = 17.7$, 4.8 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.64 – 2.48 (m, 2H), 2.02 – 1.83 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.50 (d, $J = 9.5$ Hz), -65.22 (d, $J = 9.7$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.7, 141.0, 140.6, 137.0, 133.4, 128.8, 128.64, 128.62, 128.5, 128.4 (q, $J = 282.6$ Hz), 128.3, 128.1, 127.1, 126.3, 47.5 (q, $J = 23.6$ Hz), 39.0, 38.6, 33.9, 27.2. HRMS (ESI): m/z calcd. for C$_{25}$H$_{24}$F$_3$O$^+$ [M + H$^+$]: 397.1774, found: 397.1779. $[\alpha]_{D}^{20}$ = 0.2 (c = 0.5, CHCl$_3$), HPLC chiralcel IC column (1% isopropanol in hexanes, 0.5 mL/min, $\lambda = 214$ nm), $t_R$ = 13.9 min (minor), 14.6 min (major), 16.5 min (minor), 18.0 min (major), 96% ee.
Control experiments

Vinyl bromide instead of vinyl iodide

NiBr₂•DME (10 mol%, 0.01 mmol, 3.1 mg), L9 (13 mol%, 0.013 mmol, 8.7 mg), Mn powder (2.0 equiv, 0.2 mmol, 11.0 mg), TBAI (1.0 equiv, 0.1 mmol, 36.9 mg) and vinyl bromide 1b (1.0 equiv, 0.1 mmol, 24.0 mg) were first combined in a 10 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N₂ (repeated for 3 times). Alkyl bromide 2a (2.0 equiv, 0.2 mmol, 53.2 mg), THF (0.45 mL) and N,N-Dimethylpropionamide (0.05 mL) were added via syringe. The tube was sealed with a Teflon lined cap and stirred at -4 °C for 20 h. The reaction mixture was then diluted with ethyl acetate (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with ethyl acetate (3 × 15 mL), the combined organic layer was dried over Na₂SO₄, filtered and concentrated under vacuum. The residue was then purified by flash column chromatography to give coupling product 3 in 81% yield (28.2 mg) with 94% ee.

HPLC DATA:

| Peak# | Ret. Time | Area | Area# |
|-------|-----------|------|-------|
| 1     | 36.147    | 1116706 | 2.828 |
| 2     | 40.100    | 38364196 | 97.172 |
| Total | 39480902  | 100.000 |       |

Supplementary Figure 2. Chiral HPLC analysis of Compound 3
Isomerization of product 3

NiBr$_2$•DME (10 mol%, 0.01 mmol, 3.1 mg), L9 (13 mol%, 0.013 mmol, 8.7 mg), Mn powder (2.0 equiv, 0.2 mmol, 11.0 mg), TBAI (1.0 equiv, 0.1 mmol, 36.9 mg) and coupling product (Z)-3 (1.0 equiv, 0.1 mmol, 34.8 mg) were firstly combined in a 10 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N$_2$ (repeated for 3 times). THF (0.45 mL) and N,N-Dimethylpropionamide (0.05 mL) were added via syringe. The tube was sealed with a Teflon lined cap and stirred at -4 ℃ for 12 h. The crude $^19$F NMR spectrum showed that no isomerized product (E)-3 was detected.

Monitoring experiment

NiBr$_2$•DME (10 mol%, 0.01 mmol, 3.1 mg), L9 (13 mol%, 0.013 mmol, 8.7 mg), Mn powder (2.0 equiv, 0.2 mmol, 11.0 mg), TBAI (1.0 equiv, 0.1 mmol, 36.9 mg) and vinyl iodide 1a (1.0 equiv, 0.1 mmol, 28.8 mg) were firstly combined in a 10 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N$_2$ (repeated for 3 times). Alkyl bromide 2b (2.0 equiv, 0.2 mmol, 59.2 mg), THF (0.45 mL) and N,N-Dimethylpropionamide (0.05 mL) were added via syringe. The tube was sealed with a Teflon lined cap and stirred at -4 ℃ for 2 h. The crude $^19$F NMR spectrum showed that trifluoromethyl iodide S6 and coupling product 32 were obtained in 36% and 43% yields respectively while 69% of 2b was remaining. The HPLC data showed that trifluoromethyl iodide S6 and trifluoromethyl bromide 2b were racemic while 32 had 94% ee value.
Supplementary Figure 3. Crude $^{19}$F NMR Spectrum (376 MHz, CDCl$_3$)

HPLC DATA:
HPLC chiralcel ODH column contacted with another ADH column (0.3% isopropanol in hexanes, 0.3 mL/min, $\lambda = 220$ nm).

Supplementary Figure 4. HPLC analysis of Compound 2b
Since 2b and S6 could not be separated by silica gel column chromatography after reaction, the mixture was analyzed by HPLC directly.

**Supplementary Figure 5.** HPLC analysis of Compound S6

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 60.401    | 9763785  | 50.187 |
| 2     | 65.103    | 9690953  | 49.813 |
| Total |           | 19454738 | 100.000|

**Supplementary Figure 6.** HPLC analysis of the reaction mixture

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 49.684    | 9265113  | 28.753 |
| 2     | 51.321    | 9076915  | 28.169 |
| 3     | 53.182    | 7061746  | 21.915 |
| 4     | 56.024    | 6819100  | 21.162 |
| Total |           | 32222874 | 100.000|
X-ray Crystallographic Data

**Compound 35:** (The crystal structure of compound 35 has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2170959). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.)

![Crystal Structure of Compound 35](image)

**Supplementary Table S7.** Crystal data and structure refinement for compound 35.

| Property                      | Value                          |
|-------------------------------|-------------------------------|
| Identification code           | jrx-171-4-100K_auto           |
| Empirical formula             | C_{26}H_{25}F_{3}FeO_{4}      |
| Formula weight                | 514.31                        |
| Temperature/K                 | 99.99(10)                     |
| Crystal system                | orthorhombic                  |
| Space group                   | P2_{1}2_{1}2_{1}              |
| a/Å                           | 5.93025(10)                   |
| b/Å                           | 10.42585(19)                  |
| c/Å                           | 36.15806(6)                   |
| α/°                           | 90                            |
| β/°                           | 90                            |
| γ/°                           | 90                            |
| Volume/Å³                     | 2235.57(7)                    |
| Z                             | 4                             |
| \(\rho_{\text{calc}}\)/g/Å³  | 1.528                         |
| \(\mu\)/mm⁻¹                 | 5.916                         |
| F(000)                        | 1064.0                        |
| Crystal size/mm³              | 0.21 × 0.17 × 0.15            |
| Radiation                     | Cu Kα (\(\lambda = 1.54184\)) |
| 2θ range for data collection/°| 8.828 to 145.808              |
| Index ranges                  | -4 ≤ h ≤ 7, -12 ≤ k ≤ 10, -42 ≤ l ≤ 43 |
| Reflections collected         | 5918                          |
| Independent reflections       | 3639 [R_{int} = 0.0288, R_{sigma} = 0.0446] |
| Data/restraints/parameters    | 3639/0/309                    |
| Goodness-of-fit on F²         | 1.035                         |
| Final R indexes [I>=2σ (I)]   | R₁ = 0.0335, wR₂ = 0.0812     |
| Final R indexes [all data]    | R₁ = 0.0377, wR₂ = 0.0836     |
| Largest diff. peak/hole / e Å³| 0.24/-0.36                    |
| Flack parameter               | -0.006(4)                     |
III. Supplementary Figures

NMR Spectra of New Compounds

Supplementary Figure 7. $^1$H NMR Spectrum of Compound L8 (500 MHz, CDCl$_3$)

Supplementary Figure 8. $^{13}$C NMR Spectrum of Compound L8 (126 MHz, CDCl$_3$)
Supplementary Figure 9. $^1$H NMR Spectrum of Compound L9 (500 MHz, CDCl$_3$)

Supplementary Figure 10. $^{13}$C NMR Spectrum of Compound L9 (126 MHz, CDCl$_3$)
Supplementary Figure 11. $^1$H NMR Spectrum of Compound S1 (500 MHz, CDCl$_3$)

Supplementary Figure 12. $^{19}$F NMR Spectrum of Compound S1 (471 MHz, CDCl$_3$)
Supplementary Figure 13. $^{13}$C NMR Spectrum of Compound S1 (126 MHz, CDCl$_3$)

Supplementary Figure 14. $^1$H NMR Spectrum of Compound S2 (500 MHz, CDCl$_3$)
Supplementary Figure 15. $^{13}$C NMR Spectrum of Compound S2 (126 MHz, CDCl$_3$)

Supplementary Figure 16. $^{1}$H NMR Spectrum of Compound S3 (500 MHz, CDCl$_3$)
Supplementary Figure 17. $^{13}$C NMR Spectrum of Compound S3 (126 MHz, CDCl$_3$)

Supplementary Figure 18. $^1$H NMR Spectrum of Compound S4 (500 MHz, CDCl$_3$)
Supplementary Figure 19. $^{19}$F NMR Spectrum of Compound S4 (471 MHz, CDCl$_3$)

Supplementary Figure 20. $^{13}$C NMR Spectrum of Compound S4 (126 MHz, CDCl$_3$)
Supplementary Figure 21. $^1$H NMR Spectrum of Compound S5 (500 MHz, CDCl$_3$)

Supplementary Figure 22. $^{13}$C NMR Spectrum of Compound S5 (126 MHz, CDCl$_3$)
**Supplementary Figure 23.** $^1$H NMR Spectrum of Compound S6 (500 MHz, CDCl$_3$)

**Supplementary Figure 24.** $^{19}$F NMR Spectrum of Compound S6 (471 MHz, CDCl$_3$)
Supplementary Figure 25. $^{13}$C NMR Spectrum of Compound S6 (126 MHz, CDCl$_3$)

Supplementary Figure 26. $^1$H NMR Spectrum of Compound 3 (500 MHz, CDCl$_3$)
Supplementary Figure 27. $^{19}$F NMR Spectrum of Compound 3 (471 MHz, CDCl$_3$)

Supplementary Figure 28. $^{13}$C NMR Spectrum of Compound 3 (126 MHz, CDCl$_3$)
Supplementary Figure 29. $^1$H NMR Spectrum of Compound 4 (400 MHz, CDCl$_3$)

Supplementary Figure 30. $^{19}$F NMR Spectrum of Compound 4 (376 MHz, CDCl$_3$)
Supplementary Figure 31. $^{13}$C NMR Spectrum of Compound 4 (101 MHz, CDCl$_3$)

Supplementary Figure 32. $^1$H NMR Spectrum of Compound 5 (400 MHz, CDCl$_3$)
Supplementary Figure 33. $^{19}$F NMR Spectrum of Compound 5 (376 MHz, CDCl$_3$)

Supplementary Figure 34. $^{13}$C NMR Spectrum of Compound 5 (101 MHz, CDCl$_3$)
Supplementary Figure 35. $^1$H NMR Spectrum of Compound 6 (500 MHz, CDCl$_3$)

Supplementary Figure 36. $^{19}$F NMR Spectrum of Compound 6 (471 MHz, CDCl$_3$)
Supplementary Figure 37. $^{13}$C NMR Spectrum of Compound 6 (126 MHz, CDCl$_3$)

Supplementary Figure 38. $^1$H NMR Spectrum of Compound 7 (400 MHz, CDCl$_3$)
Supplementary Figure 39. $^{19}$F NMR Spectrum of Compound 7 (376 MHz, CDCl$_3$)

Supplementary Figure 40. $^{13}$C NMR Spectrum of Compound 7 (151 MHz, CDCl$_3$)
Supplementary Figure 41. $^1$H NMR Spectrum of Compound 8 (400 MHz, CDCl$_3$)

Supplementary Figure 42. $^{19}$F NMR Spectrum of Compound 8 (376 MHz, CDCl$_3$)
Supplementary Figure 43. $^{13}$C NMR Spectrum of Compound 8 (101 MHz, CDCl$_3$)

Supplementary Figure 44. $^1$H NMR Spectrum of Compound 9 (500 MHz, CDCl$_3$)
Supplementary Figure 45. $^{19}$F NMR Spectrum of Compound 9 (471 MHz, CDCl$_3$)

Supplementary Figure 46. $^{13}$C NMR Spectrum of Compound 9 (126 MHz, CDCl$_3$)
Supplementary Figure 47. $^1$H NMR Spectrum of Compound 10 (500 MHz, CDCl$_3$)

Supplementary Figure 48. $^{19}$F NMR Spectrum of Compound 10 (471 MHz, CDCl$_3$)
Supplementary Figure 49. $^{13}$C NMR Spectrum of Compound 10 (126 MHz, CDCl$_3$)

Supplementary Figure 50. $^1$H NMR Spectrum of Compound 11 (500 MHz, CDCl$_3$)
Supplementary Figure 51. $^{19}$F NMR Spectrum of Compound 11 (471 MHz, CDCl$_3$)

Supplementary Figure 52. $^{13}$C NMR Spectrum of Compound 11 (126 MHz, CDCl$_3$)
Supplementary Figure 53. $^1$H NMR Spectrum of Compound 12 (500 MHz, CDCl$_3$)

Supplementary Figure 54. $^{19}$F NMR Spectrum of Compound 12 (471 MHz, CDCl$_3$)
Supplementary Figure 55. $^{13}$C NMR Spectrum of Compound 12 (126 MHz, CDCl$_3$)

Supplementary Figure 56. $^1$H NMR Spectrum of Compound 13 (400 MHz, CDCl$_3$)
Supplementary Figure 57. $^{19}$F NMR Spectrum of Compound 13 (376 MHz, CDCl$_3$)

Supplementary Figure 58. $^{13}$C NMR Spectrum of Compound 13 (101 MHz, CDCl$_3$)
Supplementary Figure 59. $^1$H NMR Spectrum of Compound 14 (500 MHz, CDCl$_3$)

Supplementary Figure 60. $^{19}$F NMR Spectrum of Compound 14 (471 MHz, CDCl$_3$)
Supplementary Figure 61. $^{13}$C NMR Spectrum of Compound 14 (126 MHz, CDCl$_3$)

Supplementary Figure 62. $^1$H NMR Spectrum of Compound 15 (500 MHz, CDCl$_3$)
Supplementary Figure 63. $^{19}$F NMR Spectrum of Compound 15 (471 MHz, CDCl$_3$)

Supplementary Figure 64. $^{13}$C NMR Spectrum of Compound 15 (126 MHz, CDCl$_3$)
Supplementary Figure 65. $^1$H NMR Spectrum of Compound 16 (500 MHz, CDCl$_3$)

Supplementary Figure 66. $^{19}$F NMR Spectrum of Compound 16 (471 MHz, CDCl$_3$)
Supplementary Figure 67. $^{13}$C NMR Spectrum of Compound 16 (126 MHz, CDCl$_3$)

Supplementary Figure 68. $^1$H NMR Spectrum of Compound 17 (500 MHz, CDCl$_3$)
Supplementary Figure 69. $^{19}\text{F}$ NMR Spectrum of Compound 17 (376 MHz, CDCl$_3$)

Supplementary Figure 70. $^{13}\text{C}$ NMR Spectrum of Compound 17 (126 MHz, CDCl$_3$)
Supplementary Figure 71. $^1$H NMR Spectrum of Compound 18 (500 MHz, CDCl$_3$)

Supplementary Figure 72. $^{19}$F NMR Spectrum of Compound 18 (471 MHz, CDCl$_3$)
**Supplementary Figure 73.** $^{13}$C NMR Spectrum of Compound 18 (126 MHz, CDCl$_3$)

**Supplementary Figure 74.** $^1$H NMR Spectrum of Compound 19 (500 MHz, CDCl$_3$)
Supplementary Figure 75. $^{19}$F NMR Spectrum of Compound 19 (471 MHz, CDCl$_3$)

Supplementary Figure 76. $^{13}$C NMR Spectrum of Compound 19 (126 MHz, CDCl$_3$)
**Supplementary Figure 77.** $^1$H NMR Spectrum of Compound 20 (500 MHz, CDCl$_3$)

**Supplementary Figure 78.** $^{19}$F NMR Spectrum of Compound 20 (376 MHz, CDCl$_3$)
Supplementary Figure 79. $^{13}$C NMR Spectrum of Compound 20 (101 MHz, CDCl$_3$)

Supplementary Figure 80. $^1$H NMR Spectrum of Compound 21 (500 MHz, CDCl$_3$)
Supplementary Figure 81. $^{19}$F NMR Spectrum of Compound 21 (471 MHz, CDCl$_3$)

Supplementary Figure 82. $^{13}$C NMR Spectrum of Compound 21 (126 MHz, CDCl$_3$)
Supplementary Figure 83. $^1$H NMR Spectrum of Compound 22 (500 MHz, CDCl$_3$)

Supplementary Figure 84. $^{19}$F NMR Spectrum of Compound 22 (376 MHz, CDCl$_3$)

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Supplementary Figure 85. $^{13}$C NMR Spectrum of Compound 22 (101 MHz, CDCl$_3$)

Supplementary Figure 86. $^1$H NMR Spectrum of Compound 23 (400 MHz, CDCl$_3$)
Supplementary Figure 87. $^{19}$F NMR Spectrum of Compound 23 (376 MHz, CDCl$_3$)

Supplementary Figure 88. $^{13}$C NMR Spectrum of Compound 23 (151 MHz, CDCl$_3$)
Supplementary Figure 89. $^1$H NMR Spectrum of Compound 24 (400 MHz, CDCl$_3$)

Supplementary Figure 90. $^{19}$F NMR Spectrum of Compound 24 (376 MHz, CDCl$_3$)
Supplementary Figure 91. $^{13}$C NMR Spectrum of Compound 24 (101 MHz, CDCl$_3$)

Supplementary Figure 92. $^1$H NMR Spectrum of Compound 25 (400 MHz, CDCl$_3$)
Supplementary Figure 93. $^{19}$F NMR Spectrum of Compound 25 (376 MHz, CDCl$_3$)

Supplementary Figure 94. $^{13}$C NMR Spectrum of Compound 25 (101 MHz, CDCl$_3$)
Supplementary Figure 95. $^1$H NMR Spectrum of Compound 26 (500 MHz, CDCl$_3$)

Supplementary Figure 96. $^{19}$F NMR Spectrum of Compound 26 (376 MHz, CDCl$_3$)
Supplementary Figure 97. $^{13}$C NMR Spectrum of Compound 26 (126 MHz, CDCl$_3$)

Supplementary Figure 98. $^1$H NMR Spectrum of Compound 27 (400 MHz, CDCl$_3$)
Supplementary Figure 99. $^{19}$F NMR Spectrum of Compound 27 (376 MHz, CDCl$_3$)

Supplementary Figure 100. $^{13}$C NMR Spectrum of Compound 27 (101 MHz, CDCl$_3$)
Supplementary Figure 101. $^1$H NMR Spectrum of Compound 28 (500 MHz, CDCl$_3$)

Supplementary Figure 102. $^{19}$F NMR Spectrum of Compound 28 (376 MHz, CDCl$_3$)
Supplementary Figure 103. $^{13}$C NMR Spectrum of Compound 28 (126 MHz, CDCl$_3$)

Supplementary Figure 104. $^1$H NMR Spectrum of Compound 29 (500 MHz, CDCl$_3$)
Supplementary Figure 105. $^{19}$F NMR Spectrum of Compound 29 (471 MHz, CDCl$_3$)

Supplementary Figure 106. $^{13}$C NMR Spectrum of Compound 29 (126 MHz, CDCl$_3$)
Supplementary Figure 107. $^1$H NMR Spectrum of Compound 30 (500 MHz, CDCl$_3$)

Supplementary Figure 108. $^{19}$F NMR Spectrum of Compound 30 (471 MHz, CDCl$_3$)
Supplementary Figure 109. $^{13}$C NMR Spectrum of Compound 30 (126 MHz, CDCl$_3$)

Supplementary Figure 110. $^1$H NMR Spectrum of Compound 31 (400 MHz, CDCl$_3$)
Supplementary Figure 111. $^{19}$F NMR Spectrum of Compound 31 (376 MHz, CDCl$_3$)

Supplementary Figure 112. $^{13}$C NMR Spectrum of Compound 31 (101 MHz, CDCl$_3$)
Supplementary Figure 113. $^1$H NMR Spectrum of Compound 32 (400 MHz, CDCl$_3$)

Supplementary Figure 114. $^{19}$F NMR Spectrum of Compound 32 (376 MHz, CDCl$_3$)
Supplementary Figure 115. $^{13}$C NMR Spectrum of Compound 32 (101 MHz, CDCl$_3$)

Supplementary Figure 116. $^1$H NMR Spectrum of Compound 33 (500 MHz, CDCl$_3$)
Supplementary Figure 117. $^{19}$F NMR Spectrum of Compound 33 (376 MHz, CDCl$_3$)

Supplementary Figure 118. $^{13}$C NMR Spectrum of Compound 33 (126 MHz, CDCl$_3$)
Supplementary Figure 119. $^1$H NMR Spectrum of Compound 34 (400 MHz, CDCl$_3$)

Supplementary Figure 120. $^{19}$F NMR Spectrum of Compound 34 (376 MHz, CDCl$_3$)
Supplementary Figure 121. $^{13}$C NMR Spectrum of Compound 34 (101 MHz, CDCl$_3$)

Supplementary Figure 122. $^1$H NMR Spectrum of Compound 35 (400 MHz, CDCl$_3$)
Supplementary Figure 123. $^{19}$F NMR Spectrum of Compound 35 (376 MHz, CDCl$_3$)

Supplementary Figure 124. $^{13}$C NMR Spectrum of Compound 35 (151 MHz, CDCl$_3$)
Supplementary Figure 125. $^1$H NMR Spectrum of Compound 36 (500 MHz, CDCl$_3$)

Supplementary Figure 126. $^{19}$F NMR Spectrum of Compound 36 (471 MHz, CDCl$_3$)
Supplementary Figure 127. $^{13}$C NMR Spectrum of Compound 36 (126 MHz, CDCl$_3$)

Supplementary Figure 128. $^1$H NMR Spectrum of Compound 37 (400 MHz, CDCl$_3$)
**Supplementary Figure 129.** $^{19}$F NMR Spectrum of Compound 37 (376 MHz, CDCl$_3$)

**Supplementary Figure 130.** $^{13}$C NMR Spectrum of Compound 37 (151 MHz, CDCl$_3$)
Supplementary Figure 131. $^1$H NMR Spectrum of Compound 38 (400 MHz, CDCl$_3$)

Supplementary Figure 132. $^{19}$F NMR Spectrum of Compound 38 (376 MHz, CDCl$_3$)
Supplementary Figure 133. $^{13}$C NMR Spectrum of Compound 38 (126 MHz, CDCl$_3$)

Supplementary Figure 134. $^1$H NMR Spectrum of Compound 39 (500 MHz, CDCl$_3$)
Supplementary Figure 135. $^{19}$F NMR Spectrum of Compound 39 (471 MHz, CDCl$_3$)

Supplementary Figure 136. $^{13}$C NMR Spectrum of Compound 39 (126 MHz, CDCl$_3$)
Supplementary Figure 137. $^1$H NMR Spectrum of Compound 40 (500 MHz, CDCl$_3$)

Supplementary Figure 138. $^{19}$F NMR Spectrum of Compound 40 (471 MHz, CDCl$_3$)
Supplementary Figure 139. $^{13}$C NMR Spectrum of Compound 40 (126 MHz, CDCl$_3$)

Supplementary Figure 140. $^1$H NMR Spectrum of Compound 41 (500 MHz, CDCl$_3$)
Supplementary Figure 141. $^{19}$F NMR Spectrum of Compound 41 (471 MHz, CDCl$_3$)

Supplementary Figure 142. $^{13}$C NMR Spectrum of Compound 41 (126 MHz, CDCl$_3$)
Supplementary Figure 143. ^1^H NMR Spectrum of Compound 42 (400 MHz, CDCl₃)

Supplementary Figure 144. ^19^F NMR Spectrum of Compound 42 (376 MHz, CDCl₃)
Supplementary Figure 145. $^{13}$C NMR Spectrum of Compound 42 (101 MHz, CDCl$_3$)

Supplementary Figure 146. $^1$H NMR Spectrum of Compound 43 (500 MHz, CDCl$_3$)
Supplementary Figure 147. $^{19}$F NMR Spectrum of Compound 43 (471 MHz, CDCl$_3$)

Supplementary Figure 148. $^{13}$C NMR Spectrum of Compound 43 (126 MHz, CDCl$_3$)
Supplementary Figure 149. $^1$H NMR Spectrum of Compound 44 (400 MHz, CDCl$_3$)

Supplementary Figure 150. $^{19}$F NMR Spectrum of Compound 44 (376 MHz, CDCl$_3$)
Supplementary Figure 151. $^{13}$C NMR Spectrum of Compound 44 (151 MHz, CDCl$_3$)

Supplementary Figure 152. $^1$H NMR Spectrum of Compound 45 (500 MHz, CDCl$_3$)
Supplementary Figure 153. $^{19}$F NMR Spectrum of Compound 45 (376 MHz, CDCl$_3$)

Supplementary Figure 154. $^{13}$C NMR Spectrum of Compound 45 (126 MHz, CDCl$_3$)
Supplementary Figure 155. $^1$H NMR Spectrum of Compound 46 (400 MHz, CDCl$_3$)

Supplementary Figure 156. $^{19}$F NMR Spectrum of Compound 46 (376 MHz, CDCl$_3$)
Supplementary Figure 157. $^{13}$C NMR Spectrum of Compound 46 (151 MHz, CDCl$_3$)

Supplementary Figure 158. $^1$H NMR Spectrum of Compound 47 (500 MHz, CDCl$_3$)
Supplementary Figure 159. $^{19}$F NMR Spectrum of Compound 47 (471 MHz, CDCl$_3$)

Supplementary Figure 160. $^{13}$C NMR Spectrum of Compound 47 (126 MHz, CDCl$_3$)
Supplementary Figure 16. $^1$H NMR Spectrum of Compound 48 (500 MHz, CDCl$_3$)

Supplementary Figure 162. $^{19}$F NMR Spectrum of Compound 48 (471 MHz, CDCl$_3$)
Supplementary Figure 163. $^{13}$C NMR Spectrum of Compound 48 (126 MHz, CDCl$_3$)

Supplementary Figure 164. $^1$H NMR Spectrum of Compound 49 (400 MHz, CDCl$_3$)
**Supplementary Figure 165.** $^{19}$F NMR Spectrum of Compound 49 (376 MHz, CDCl$_3$)

**Supplementary Figure 166.** $^{13}$C NMR Spectrum of Compound 49 (126 MHz, CDCl$_3$)
Supplementary Figure 167. $^1$H NMR Spectrum of Compound 50-major (500 MHz, CDCl$_3$)

Supplementary Figure 168. $^{19}$F NMR Spectrum of Compound 50-major (471 MHz, CDCl$_3$)
Supplementary Figure 169. $^{13}$C NMR Spectrum of Compound 50-major (126 MHz, CDCl$_3$)

Supplementary Figure 170. $^1$H NMR Spectrum of Compound 50-minor (400 MHz, CDCl$_3$)
Supplementary Figure 171. $^{19}$F NMR Spectrum of Compound 50-minor (471 MHz, CDCl$_3$)

Supplementary Figure 172. $^{13}$C NMR Spectrum of Compound 50-minor (126 MHz, CDCl$_3$)
**Supplementary Figure 173.** $^1$H NMR Spectrum of Compound 51 (500 MHz, CDCl$_3$)

**Supplementary Figure 174.** $^{19}$F NMR Spectrum of Compound 51 (471 MHz, CDCl$_3$)
Supplementary Figure 175. $^{13}$C NMR Spectrum of Compound 51 (126 MHz, CDCl$_3$)

Supplementary Figure 176. $^1$H NMR Spectrum of Compound 52 (400 MHz, CDCl$_3$)
Supplementary Figure 177. $^{19}$F NMR Spectrum of Compound 52 (376 MHz, CDCl$_3$)

Supplementary Figure 178. $^{13}$C NMR Spectrum of Compound 52 (126 MHz, CDCl$_3$)
Supplementary Figure 179. $^1$H NMR Spectrum of Compound 53 (400 MHz, CDCl$_3$)

Supplementary Figure 180. $^{19}$F NMR Spectrum of Compound 53 (376 MHz, CDCl$_3$)
Supplementary Figure 181. $^{13}$C NMR Spectrum of Compound 53 (101 MHz, CDCl$_3$)

Supplementary Figure 182. $^1$H NMR Spectrum of Compound 54 (400 MHz, CDCl$_3$)
Supplementary Figure 183. $^{19}$F NMR Spectrum of Compound 54 (376 MHz, CDCl$_3$)

Supplementary Figure 184. $^{13}$C NMR Spectrum of Compound 54 (126 MHz, CDCl$_3$)
HPLC Data

Supplementary Figure 185. Chiral HPLC analysis of Compound 3
Supplementary Figure 186. Chiral HPLC analysis of Compound 4
### Supplementary Figure 187. Chiral HPLC analysis of Compound 5

| Peak# | Ret. Time | Area (×10^6) | Area% |
|-------|-----------|--------------|-------|
| 1     | 10.265    | 3344965      | 49.846|
| 2     | 15.640    | 3365651      | 50.154|
| Total |           | 6710616      | 100.000|

| Peak# | Ret. Time | Area (×10^6) | Area% |
|-------|-----------|--------------|-------|
| 1     | 10.163    | 216988       | 2.358 |
| 2     | 15.412    | 8985974      | 97.642|
| Total |           | 9202962      | 100.000|
### Supplementary Figure 188. Chiral HPLC analysis of Compound 6

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 14.481    | 34199150 | 49.953 |
| 2     | 20.071    | 34263567 | 50.047 |
| Total |           | 68462717 | 100.000 |

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 14.951    | 573312 | 2.440  |
| 2     | 20.348    | 22921705 | 97.560 |
| Total |           | 23495017 | 100.000 |
| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 7.434     | 1859711| 50.075 |
| 2     | 8.964     | 1854129| 49.925 |
| Total |           | 3713840| 100.000|

**Supplementary Figure 189.** Chiral HPLC analysis of Compound 7
| Peak# | Ret. Time | Area   | Area#  |
|------|-----------|--------|--------|
| 1    | 8.169     | 1310475| 49.799 |
| 2    | 9.496     | 1321032| 50.201 |
| Total|           | 2631507| 100.000|

Supplementary Figure 190. Chiral HPLC analysis of Compound 8
### Supplementary Figure 191. Chiral HPLC analysis of Compound 9

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 9.492     | 3099415  | 49.962 |
| 2     | 10.995    | 3104175  | 50.038 |
| Total |           | 6203590  | 100.000|

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 9.669     | 449254   | 2.925  |
| 2     | 11.185    | 14909908 | 97.075 |
| Total |           | 15359162 | 100.000|

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### Supplementary Figure 192. Chiral HPLC analysis of Compound 10

| Peak# | Ret. Time | Area  | Area#  |
|-------|-----------|-------|--------|
| 1     | 6.115     | 8465721 | 49.702 |
| 2     | 7.357     | 8567130 | 50.298 |
| Total |           | 17032851 | 100.000 |

| Peak# | Ret. Time | Area  | Area#  |
|-------|-----------|-------|--------|
| 1     | 6.612     | 411026 | 2.433  |
| 2     | 8.104     | 16481241 | 97.567 |
| Total |           | 16892267 | 100.000 |
**Supplementary Figure 193.** Chiral HPLC analysis of Compound 11
| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 6.752     | 1955398 | 50.171 |
| 2     | 7.718     | 1942084 | 49.829 |
| Total |           | 3897482 | 100.000|

**Supplementary Figure 194.** Chiral HPLC analysis of Compound 12
Supplementary Figure 195. Chiral HPLC analysis of Compound 13
### Supplementary Figure 196. Chiral HPLC analysis of Compound 14

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 11.647    | 12925962 | 49.584 |
| 2     | 22.271    | 13142992 | 50.416 |
| Total |           | 26068955 | 100.000|

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 11.715    | 121589   | 1.923  |
| 2     | 21.566    | 6201518  | 98.077 |
| Total |           | 6323107  | 100.000|
Supplementary Figure 197. Chiral HPLC analysis of Compound 15
Supplementary Figure 198. Chiral HPLC analysis of Compound 16
| Peak# | Ret. Time | Area   | Area#  |
|------|-----------|--------|--------|
| 1    | 19.161    | 6489108| 49.776 |
| 2    | 21.000    | 6547627| 50.224 |
| Total|           | 13036734| 100.000|

**Supplementary Figure 199.** Chiral HPLC analysis of Compound 17
Supplementary Figure 200. Chiral HPLC analysis of Compound 18
### Chiral HPLC Analysis of Compound 19

**Supplementary Figure 201.** Chiral HPLC analysis of Compound 19

| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 9.259     | 2018012 | 49.686 |
| 2     | 9.954     | 2043492 | 50.314 |
| Total |           | 4061504 | 100.000 |

| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 9.149     | 120969  | 3.803  |
| 2     | 9.834     | 3059532 | 96.197 |
| Total |           | 3180501 | 100.000 |
Supplementary Figure 202. Chiral HPLC analysis of Compound 20
### Supplementary Figure 203. Chiral HPLC analysis of Compound 21

#### Table 1

| Peak# | Ret. Time | Area    | Area#   |
|-------|-----------|---------|---------|
| 1     | 8.232     | 3758044 | 49.596  |
| 2     | 9.955     | 3819232 | 50.404  |
| Total |           | 7577276 | 100.000 |

#### Table 2

| Peak# | Ret. Time | Area    | Area#   |
|-------|-----------|---------|---------|
| 1     | 7.993     | 506047  | 4.067   |
| 2     | 9.587     | 11936045| 95.933  |
| Total |           | 12442092| 100.000 |
### Supplementary Figure 204. Chiral HPLC analysis of Compound 22

**Table 1:**

| Peak# | Ret. Time | Area   | Area#  |
|------|-----------|--------|--------|
| 1    | 6.075     | 1415000| 49.572 |
| 2    | 6.672     | 1439445| 50.428 |
| Total|           | 2854445| 100.000|

**Table 2:**

| Peak# | Ret. Time | Area   | Area#  |
|------|-----------|--------|--------|
| 1    | 6.086     | 32043  | 1.410  |
| 2    | 6.667     | 2239689| 98.590 |
| Total|           | 2271731| 100.000|
Supplementary Figure 205. Chiral HPLC analysis of Compound 23
Supplementary Figure 206. Chiral HPLC analysis of Compound 24
| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 4.965     | 2968081| 50.535 |
| 2     | 5.589     | 2905217| 49.465 |
| Total |           | 5873298| 100.000|

**Supplementary Figure 207.** Chiral HPLC analysis of Compound 25
### Supplementary Figure 208. Chiral HPLC analysis of Compound 26

| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 14.858    | 1403644 | 5.034  |
| 2     | 15.887    | 26478207| 94.966 |
| Total |           | 27881851| 100.000|

| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 14.875    | 6502124 | 50.253 |
| 2     | 15.941    | 6436708 | 49.747 |
| Total |           | 12938832| 100.000|
| Peak# | Ret. Time | Area     | Area#    |
|-------|-----------|----------|----------|
| 1     | 22.345    | 7836214  | 49.667   |
| 2     | 24.107    | 7941404  | 50.333   |
| Total |           | 15777618 | 100.000  |

| Peak# | Ret. Time | Area     | Area#    |
|-------|-----------|----------|----------|
| 1     | 21.394    | 489399   | 2.102    |
| 2     | 22.951    | 22795824 | 97.898   |
| Total |           | 23285223 | 100.000  |

**Supplementary Figure 209.** Chiral HPLC analysis of Compound 27
### Table 1: Chiral HPLC Analysis of Compound 28

| Peak# | Ret. Time | Area     | Area\# |
|-------|-----------|----------|--------|
| 1     | 20.610    | 9489315  | 50.324 |
| 2     | 22.591    | 9367093  | 49.676 |
| Total |           | 18856408 | 100.000|

### Table 2: Chiral HPLC Analysis of Compound 28

| Peak# | Ret. Time | Area     | Area\# |
|-------|-----------|----------|--------|
| 1     | 20.947    | 476226   | 2.320  |
| 2     | 23.032    | 20050028 | 97.680 |
| Total |           | 20526254 | 100.000|

**Supplementary Figure 210.** Chiral HPLC analysis of Compound 28
Supplementary Figure 211. Chiral HPLC analysis of Compound 29
**Supplementary Figure 212.** Chiral HPLC analysis of Compound 30
### Supplementary Figure 213. Chiral HPLC analysis of Compound 31

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.167     | 13485600 | 49.921 |
| 2     | 20.931    | 13528529 | 50.079 |
| Total |           | 27014129 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.154     | 34830380 | 96.851 |
| 2     | 21.521    | 1132354  | 3.149  |
| Total |           | 35962735 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.167     | 13485600 | 49.921 |
| 2     | 20.931    | 13528529 | 50.079 |
| Total |           | 27014129 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.154     | 34830380 | 96.851 |
| 2     | 21.521    | 1132354  | 3.149  |
| Total |           | 35962735 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.167     | 13485600 | 49.921 |
| 2     | 20.931    | 13528529 | 50.079 |
| Total |           | 27014129 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.154     | 34830380 | 96.851 |
| 2     | 21.521    | 1132354  | 3.149  |
| Total |           | 35962735 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.167     | 13485600 | 49.921 |
| 2     | 20.931    | 13528529 | 50.079 |
| Total |           | 27014129 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 8.154     | 34830380 | 96.851 |
| 2     | 21.521    | 1132354  | 3.149  |
| Total |           | 35962735 | 100.000 |

**Supplementary Figure 213.** Chiral HPLC analysis of Compound 31
| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 23.970    | 17666673 | 49.675 |
| 2     | 25.950    | 17897874 | 50.325 |
| Total |           | 35564548 | 100.000|

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 23.764    | 33326410 | 97.074 |
| 2     | 26.350    | 1004644  | 2.926  |
| Total |           | 34331053 | 100.000|

**Supplementary Figure 214.** Chiral HPLC analysis of Compound 32
Supplementary Figure 215. Chiral HPLC analysis of Compound 33
Supplementary Figure 216. Chiral HPLC analysis of Compound 34

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 16.940    | 25104090 | 97.883 |
| 2     | 18.854    | 543044   | 2.117  |
| Total |           | 25647135 | 100.000|

| Peak# | Ret. Time | Area     | Area#  |
|-------|-----------|----------|--------|
| 1     | 17.181    | 3423703  | 49.964 |
| 2     | 19.004    | 3428602  | 50.036 |
| Total |           | 6852305  | 100.000|
### Supplementary Figure 217. Chiral HPLC analysis of Compound 35

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 15.952    | 30106112 | 49.941 |
| 2     | 19.242    | 30176807 | 50.059 |
| Total |           | 60282919 | 100.000 |

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| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 16.084    | 448656 | 2.465  |
| 2     | 19.362    | 17755048 | 97.535 |
| Total |           | 18203704 | 100.000 |
### Supplementary Figure 218. Chiral HPLC analysis of Compound 36

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 15.291    | 2907792| 50.180 |
| 2     | 24.911    | 2886910| 49.820 |
| Total |           | 5794702| 100.000|

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 15.538    | 964868 | 4.062  |
| 2     | 24.798    | 22788125| 95.938 |
| Total |           | 23752993| 100.000|
Supplementary Figure 219. Chiral HPLC analysis of Compound 37
Supplementary Figure 220. Chiral HPLC analysis of Compound 38
### Supplementary Figure 221. Chiral HPLC analysis of Compound 39

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 36.572    | 2511665| 25.371 |
| 2     | 38.510    | 2512981| 25.385 |
| 3     | 42.934    | 2436857| 24.616 |
| 4     | 51.435    | 2438153| 24.629 |
| Total |           | 9899655| 100.000|

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 36.245    | 4877380| 48.291 |
| 2     | 38.187    | 181739 | 1.799  |
| 3     | 42.576    | 4879868| 48.316 |
| 4     | 51.050    | 161013 | 1.594  |
| Total |           | 1010000| 100.000|
Supplementary Figure 222. Chiral HPLC analysis of Compound 40
### Supplementary Figure 223. Chiral HPLC analysis of Compound 41

#### Table 1

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 42.141    | 2664704| 49.886 |
| 2     | 44.609    | 2676866| 50.114 |
| Total |           | 5341569| 100.000|

#### Table 2

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 43.089    | 4517879| 97.127 |
| 2     | 45.629    | 133626 | 2.873  |
| Total |           | 4651505| 100.000|
### Supplementary Figure 224. Chiral HPLC analysis of Compound 42

| Peak# | Ret. Time | Area  | Area#  |
|-------|-----------|-------|--------|
| 1     | 88.065    | 6833138 | 49.804 |
| 2     | 116.354   | 6886839 | 50.196 |
| Total |           | 13719977 | 100.000 |

- **Peak#**
- **Ret. Time**
- **Area**
- **Area#**
| Peak# | Ret. Time | Area      | Area#  |
|------|-----------|-----------|--------|
| 1    | 7.190     | 3941262   | 50.623 |
| 2    | 7.931     | 3844190   | 49.377 |
| Total|           | 7785452   | 100.000|

| Peak# | Ret. Time | Area      | Area#  |
|------|-----------|-----------|--------|
| 1    | 7.144     | 16092136  | 97.795 |
| 2    | 7.891     | 362876    | 2.205  |
| Total|           | 16455012  | 100.000|

**Supplementary Figure 225.** Chiral HPLC analysis of Compound 43
### Supplementary Figure 226. Chiral HPLC analysis of Compound 44

| Peak# | Ret. Time | Area       | Area#  |
|-------|-----------|------------|--------|
| 1     | 20.539    | 20155238   | 49.942 |
| 2     | 23.141    | 20202068   | 50.058 |
| Total |           | 40357305   | 100.000|

| Peak# | Ret. Time | Area       | Area#  |
|-------|-----------|------------|--------|
| 1     | 19.620    | 14593824   | 97.163 |
| 2     | 22.249    | 426076     | 2.837  |
| Total |           | 15019900   | 100.000|
Supplementary Figure 227. Chiral HPLC analysis of Compound 45
Supplementary Figure 228. Chiral HPLC analysis of Compound 46
Supplementary Figure 229. Chiral HPLC analysis of Compound 47
Supplementary Figure 230. Chiral HPLC analysis of Compound 48
### Supplementary Figure 231. Chiral HPLC analysis of Compound 49

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 23.823    | 4062203| 49.783 |
| 2     | 27.112    | 4097661| 50.217 |
| Total |           | 8159864| 100.000|

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 24.932    | 170330 | 2.488  |
| 2     | 28.030    | 6675492| 97.512 |
| Total |           | 6845822| 100.000|
Supplementary Figure 232. Chiral HPLC analysis of Compound 50-major
### Peak Analysis

| Peak# | Ret. Time | Area   | Area#  |
|-------|-----------|--------|--------|
| 1     | 10.514    | 1674654| 49.800 |
| 2     | 16.708    | 1688120| 50.200 |
| Total |           | 3362774| 100.000|

**Supplementary Figure 233.** Chiral HPLC analysis of Compound 50-minor
Supplementary Figure 234. Chiral HPLC analysis of Compound 51
| Peak# | Ret. Time | Area   | Area#  |
|------|-----------|--------|--------|
| 1    | 14.765    | 947817 | 49.833 |
| 2    | 15.596    | 954165 | 50.167 |
| Total|           | 1901983| 100.000|

| Peak# | Ret. Time | Area   | Area#  |
|------|-----------|--------|--------|
| 1    | 14.923    | 95405  | 3.181  |
| 2    | 15.848    | 2904149| 96.819 |
| Total|           | 2999555| 100.000|

**Supplementary Figure 235.** Chiral HPLC analysis of Compound 52
Supplementary Figure 236. Chiral HPLC analysis of Compound 53
### Supplementary Figure 237. Chiral HPLC analysis of Compound 54

#### Table 1: Retention Time and Area for Compound 54

| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 14.058    | 211373  | 1.347  |
| 2     | 14.880    | 7804678 | 49.721 |
| 3     | 16.815    | 7488852 | 47.709 |
| 4     | 18.339    | 191945  | 1.223  |
| Total |           | 15696848| 100.000|

### Supplementary Figure 237. Chiral HPLC analysis of Compound 54

#### Table 2: Retention Time and Area for Compound 54

| Peak# | Ret. Time | Area    | Area#  |
|-------|-----------|---------|--------|
| 1     | 13.866    | 9438    | 0.221  |
| 2     | 14.645    | 3976842 | 93.039 |
| 3     | 16.544    | 74134   | 1.734  |
| 4     | 17.951    | 213948  | 5.005  |
| Total |           | 4274362 | 100.000|
IV. Supplementary References

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