Supporting information

Overcoming O-H Insertion to Para-Selective C–H Functionalization of Free Phenols: Rh(II)/Xantphos Catalyzed Geminal-Difunctionalization of Diazo Compounds

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1. General Information

Unless otherwise noted, all the reactions were performed using standard Schlenk techniques under an atmosphere of argon or in glovebox and glassware were dried in an oven before use. All reagents were purchased from commercial sources and were used directly without further purification or prepared as described in the literature. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on Varian 400 MHz, Agilent 400 MHz or Bruker 400 MHz spectrometers. Chemical shifts ($\delta$ values) were reported in ppm relative to internal TMS ($^1$H NMR: 0.000 ppm) or CDCl$_3$ ($^1$H NMR: 7.260 ppm; $^{13}$C NMR: 77.16 ppm), respectively. The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Flash column chromatography was performed using 200-300 mesh silicagel. IR spectra were obtained on Bruker Tensor 27 instruments with Bruker Platinum ATR accessory. HRMS (ESI) were determined on Agilent 6224 TOF LC/MS. Shimadzu GC-2014 spectrometer using flame ionization detector and the heating procedure was established as follows: initial temperature, 50 °C, hold time, 0.1 min; heating rate 15 °C/min, reach temperature 150 °C, hold time, 3 min; heating rate 30 °C/min, final temperature 280 °C, hold time, 7 min. HPLC analysis were performed on a JASCO 2089 liquid chromatograph, a Shimadzu HPLC system equipped with Daicel chiral-stationary-phase columns, UtiMate 3000 RS Column Compartment.
2. Preparation of Diazo Substrates

![Diazo substrates diagram]

Figure S1. Diazo substrates

Phenol Compounds 1 are commercially available. Diazo compounds 2a-2s were synthesized according to the following General Procedure and 2a, 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2i, 2j, 2k, 2l, 2m, 2n, 2o, 2p, 2q, 2r, 2s are known compounds that characterization matched the data previously reported. Allylic substrates 3 was purchased.

**General Procedure for Preparation of Diazoesters**

According to the literature methods: To a solution of arylacetate (1.0 eq.) and 4-methylbenzenesulfonyl azide (1.2 eq.) in dry CH$_3$CN (0.2 M) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.5 eq.) at 0 °C. The resultant mixture was stirred at room temperature. Upon consumption of the starting material (monitored by TLC), the reaction mixture
was quenched with saturated aqueous NH$_4$Cl (15.0 mL) and extracted with CH$_2$Cl$_2$ three times. The combined organic phase was washed with saturated aqueous NaHCO$_3$, saturated brine, and dried over anhydrous Na$_2$SO$_4$. Then concentration was conducted under reduced pressure. The crude product obtained was purified by flash column chromatography on silica gel to give the desired compound.

\[
\text{Methyl 2-(3-cyanophenyl)-2-diazoacetate (2f)}
\]

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow solid, (882.9 mg, 81% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (s, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.52–7.41 (m, 2H), 3.89 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.6, 129.6, 128.9, 127.8, 127.2, 126.8, 118.4, 113.3, 52.3 ppm.

HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{10}$H$_8$N$_3$O$_2$, 202.0611; found: 202.0612.

### 3. Optimization of the Conditions

**Table S1. Screening of the base$^a$**

| Entry | Base            | 4aa$^b$ | 5aa$^b$ | 6aa$^b$ |
|-------|----------------|---------|---------|---------|
| 1     | KO'Bu          | 0       | 0       | 0       |
| 2     | KOH            | 82      | 24      | 0       |
| 3     | CsOH·H$_2$O    | 82      | 8       | 8       |
| 4     | Cs$_2$CO$_3$   | 42      | 0       | 85      |
| 5     | K$_2$CO$_3$    | 71      | 32      | 0       |
| 6     | Na$_2$CO$_3$   | 31      | 26      | 0       |
| 7     | Li$_2$CO$_3$   | 95      | 5       | 0       |
Unless otherwise noted, all reactions were carried out using 1a (0.375 mmol, 1.5 eq.), 2a (0.25 mmol, 1.0 eq.), 3 (0.75 mmol, 3.0 eq.), Rh2(OPiv)4 (1.0 mol%), Xantphos (1.5 mol%) and base (3.5 eq.) in MeCN (2.0 mL) under Ar at 60 °C for 6.0 h. b GC yields. Yields for 4aa were calculated based on 1a as a limiting substrate. Yields for 5aa and 6aa were calculated based on 2a as a limiting substrate. c 1.0 eq. Cs2CO3 was used. d 2.0 eq. Cs2CO3 was used.

4. Typical Experimental Procedure for the Multicomponent Reaction

In an oven-dried 10 mL sealed tube equipped with a stir bar was added Rh2(OPiv)4 (1.5 mg, 2.5 x 10^-3 mmol, 1.0 mol%), Xantphos (2.2 mg, 3.75 x 10^-3 mmol, 1.5 mol%), Cs2CO3 (285.0 mg, 0.875 mmol, 3.5 eq.), phenol 1 (0.375 mmol, 1.5 eq.) under dry argon atmosphere. Then, anhydrous CH3CN (2.0 mL), allyl ethyl carbonate 3 (0.75 mmol, 3.0 eq.) and diazo compound 2 (0.25 mmol, 1.0 eq.) were introduced, respectively. The resulting mixture was stirred at 60 °C for 6.0 h. After cooling to ambient temperature, the mixture was filtered, and the clear filtrate was collected. After removing the solvents in vacuo, the crude product was purified by flash column chromatography on silica gel to give the desired product 6.

Methyl 2-(4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6aa)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil (67.0 mg, 83% yield).
**1H NMR** (400 MHz, CDCl₃) δ 7.31–7.15 (m, 7H), 6.84 (d, J = 8.8 Hz, 2H), 6.16–5.94 (m, 1H), 5.70–5.50 (m, 1H), 5.40 (d, J = 17.2 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 4.99–4.87 (m, 2H), 4.51 (d, J = 4.8 Hz, 2H), 3.67 (s, 3H), 3.19–3.08 (m, 2H) ppm.

**13C NMR** (100 MHz, CDCl₃) δ 174.8, 157.4, 142.9, 134.7, 134.4, 133.4, 130.1, 128.9, 127.9, 126.8, 118.3, 117.8, 114.0, 68.8, 59.7, 52.4, 43.0 ppm.

**IR** (neat) ν 2949, 1728, 1607, 1509, 1446, 1219, 1179, 995, 918, 828, 699, 532 cm⁻¹.

**HRMS-ESI** (m/z): [M + Na]^+ calcd for C₂₁H₂₂O₃Na, 345.1461; found: 345.1461.

![Methyl 2-(4-(allyloxy)-3-(tert-butyl)phenyl)-2-phenylpent-4-enoate (6ba)](image)

**Methyl 2-(4-(allyloxy)-3-(tert-butyl)phenyl)-2-phenylpent-4-enoate (6ba)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (68.2 mg, 72% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.32–7.17 (m, 6H), 7.04 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.20–5.99 (m, 1H), 5.67–5.53 (m, 1H), 5.44 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.00–4.86 (m, 2H), 4.55 (d, J = 4.0 Hz, 2H), 3.68 (s, 3H), 3.14 (d, J = 6.8 Hz, 2H), 1.34 (s, 9H) ppm.

**13C NMR** (100 MHz, CDCl₃) δ 175.1, 156.2, 143.1, 137.3, 134.7, 133.7, 129.0, 127.8, 127.7, 127.5, 126.7, 118.1, 117.1, 111.6, 68.9, 60.0, 52.3, 43.1, 35.1, 29.9 ppm (one sp² C-atom missing due to overlap).

**IR** (neat) ν 2951, 1729, 1494, 1447, 1359, 1218, 1093, 995, 916, 812, 699 cm⁻¹.

**HRMS-ESI** (m/z): [M + Na]^+ calcd for C₂₅H₃₀O₃Na, 401.2087; found: 401.2088.

![Methyl 2-(3-allyl-4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6ca)](image)

**Methyl 2-(3-allyl-4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6ca)**
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (66.8 mg, 74% yield).

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3 \ \delta \ 7.28-7.22 \ (m, \ 5H), \ 7.07-7.05 \ (m, \ 2H), \ 6.75 \ (d, \ J = 8.0 \text{ Hz}, \ 1H), \ 6.15-5.82 \ (m, \ 2H), \ 5.68-5.50 \ (m, \ 1H), \ 5.41 \ (d, \ J = 17.2 \text{ Hz}, \ 1H), \ 5.25 \ (d, \ J = 10.4 \text{ Hz}, \ 1H), \ 5.09-\
4.84 \ (m, \ 4H), \ 4.60-4.41 \ (m, \ 2H), \ 3.67 \ (s, \ 3H), \ 3.37 \ (d, \ J = 6.8 \text{ Hz}, \ 2H), \ 3.20-3.05 \ (m, \ 2H) \text{ ppm.} \]

\[ ^{13}C \text{NMR} \ (100 \text{ MHz, CDCl}_3 \ \delta \ 174.9, \ 155.2, \ 142.9, \ 137.0, \ 134.5, \ 134.3, \ 133.6, \ 130.7, \ 129.0, \ 128.2, \ 127.9, \ 127.8, \ 126.8, \ 118.2, \ 117.0, \ 115.4, \ 110.9, \ 68.8, \ 59.8, \ 52.3, \ 43.0, \ 34.6 \text{ ppm.} \]

\[ \text{IR (neat) } \nu \ 2949, \ 1728, \ 1638, \ 1497, \ 1433, \ 1222, \ 1132, \ 995, \ 914, \ 811, \ 699 \text{ cm}^{-1} \]

\[ \text{HRMS-ESI (m/z): } [M + Na]^+ \text{ calcd for } C_{24}H_{26}O_3Na, \ 385.1774; \text{ found: 385.1776.} \]

**Methyl 2-(4-(allyloxy)-3-benzylyphenyl)-2-phenylpent-4-enoate (6da)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (87.6 mg, 85% yield).

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3 \ \delta \ 7.26-7.19 \ (m, \ 7H), \ 7.16-7.09 \ (m, \ 3H), \ 7.07-7.04 \ (m, \ 2H), \ 6.79-6.68 \ (m, \ 1H), \ 6.05-5.90 \ (m, \ 1H), \ 5.65-5.47 \ (m, \ 1H), \ 5.33 \ (dd, \ J = 17.2, \ 1.6 \text{ Hz}, \ 1H), \ 5.20 \ (dd, \ J = 10.8, \ 1.6 \text{ Hz}, \ 1H), \ 4.95-4.82 \ (m, \ 2H), \ 4.46 \ (d, \ J = 4.8 \text{ Hz}, \ 2H), \ 3.99-3.89 \ (m, \ 2H), \ 3.62 \ (s, \ 3H), \ 3.10 \ (d, \ J = 6.8 \text{ Hz}, \ 2H) \text{ ppm.} \]

\[ ^{13}C \text{NMR} \ (100 \text{ MHz, CDCl}_3 \ \delta \ 174.8, \ 155.2, \ 142.9, \ 141.1, \ 134.4, \ 134.2, \ 133.5, \ 131.6, \ 129.2, \ 129.0, \ 128.9, \ 128.2, \ 127.84, \ 127.80, \ 126.8, \ 125.8, \ 118.2, \ 117.1, \ 110.9, \ 68.8, \ 59.7, \ 52.3, \ 42.9, \ 36.4 \text{ ppm.} \]

\[ \text{IR (neat) } \nu \ 3025, \ 2948, \ 1728, \ 1640, \ 1602, \ 1495, \ 1447, \ 1223, \ 1122, \ 996, \ 918, \ 729, \ 697 \text{ cm}^{-1}. \]

\[ \text{HRMS-ESI (m/z): } [M + Na]^+ \text{ calcd for } C_{28}H_{38}O_3Na, \ 435.1931; \text{ found: 435.1933.} \]
Methyl 2-(6-(allyloxy)-[1,1'-biphenyl]-3-yl)-2-phenylpent-4-enoate (6ea)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (87.5 mg, 88% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 7.2$ Hz, 2H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.32–7.24 (m, 6H), 7.24–7.16 (m, 2H), 6.87 (d, $J = 8.4$ Hz, 1H), 6.04–5.86 (m, 1H), 5.77–5.49 (m, 1H), 5.31 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.18 (dd, $J = 10.4$, 1.6 Hz, 1H), 4.95 (d, $J = 12.4$ Hz, 2H), 4.99–4.89 (m, 2H), 3.68 (s, 3H), 3.62–3.11 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.7, 154.3, 142.8, 138.5, 134.8, 134.4, 133.3, 131.8, 130.1, 129.7, 129.1, 128.9, 127.9, 126.94, 126.87, 118.3, 116.9, 112.0, 69.1, 59.8, 52.4, 43.0 ppm.

IR (neat) $\nu$ 2948, 1727, 1601, 1486, 1445, 1217, 995, 917, 812, 770, 697 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{27}$H$_{26}$O$_3$Na, 421.1774; found: 421.1777.

Methyl 2-(4-(allyloxy)-3-methoxyphenyl)-2-phenylpent-4-enoate (6fa)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), yellow oil (51.9 mg, 59% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.21 (m, 5H), 6.85–6.77 (m, 3H), 6.16–6.00 (m, 1H), 5.67–5.49 (m, 1H), 5.40 (d, $J = 17.2$ Hz, 1H), 5.28 (d, $J = 10.4$ Hz, 1H), 4.98–4.90 (m, 2H), 4.60 (d, $J = 5.2$ Hz, 2H), 3.75 (s, 3H), 3.69 (s, 3H), 3.20–3.08 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.7, 148.6, 147.0, 142.8, 135.1, 134.4, 133.4, 129.0, 127.8, 126.8, 121.1, 118.2, 118.1, 113.3, 112.3, 69.8, 60.0, 56.0, 52.4, 43.0 ppm.

IR (neat) $\nu$ 2949, 1728, 1588, 1511, 1446, 1253, 1215, 1145, 994, 918, 804, 699 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{22}$H$_{24}$O$_4$Na, 375.1567; found: 375.1568.
Methyl 2-(4-(allyloxy)-3-chlorophenyl)-2-phenylpent-4-enoate (6ga)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (50.2 mg, 56% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.20 (m, 6H), 7.09 (dd, $J = 8.8$, 2.0 Hz, 1H), 6.83 (d, $J = 8.8$ Hz, 1H), 6.13–5.98 (m, 1H), 5.63–5.50 (m, 1H), 5.46 (d, $J = 17.2$ Hz, 1H), 5.30 (d, $J = 10.8$ Hz, 1H), 4.98–4.89 (m, 2H), 4.59 (d, $J = 4.4$ Hz, 2H), 3.69 (s, 3H), 3.11 (d, $J = 6.8$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.3, 152.9, 142.3, 135.8, 134.0, 132.7, 131.0, 128.8, 128.4, 128.1, 127.1, 122.3, 118.7, 118.0, 112.8, 69.8, 59.6, 52.6, 42.9 ppm.

IR (neat) $\nu$ 2950, 1729, 1597, 1492, 1287, 1215, 1047, 995, 921, 784, 697 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{21}$H$_{21}$O$_3$ClNa, 379.1071; found: 379.1073.

Methyl 2-(4-(allyloxy)-3-bromophenyl)-2-phenylpent-4-enoate (6ha)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (69.9 mg, 70% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 2.4$ Hz, 1H), 7.33–7.18 (m, 5H), 7.13 (dd, $J = 8.8$, 2.4 Hz, 1H), 6.80 (d, $J = 8.8$ Hz, 1H), 6.11–5.98 (m, 1H), 5.63–5.51 (m, 1H), 5.47 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.30 (dd, $J = 10.8$, 1.6 Hz, 1H), 5.00–4.88 (m, 2H), 4.66–4.52 (m, 2H), 3.69 (s, 3H), 3.11 (d, $J = 6.8$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.3, 153.8, 142.3, 136.2, 133.91, 133.88, 132.6, 129.2, 128.7, 128.1, 127.1, 118.7, 117.9, 112.5, 111.6, 69.7, 59.5, 52.6, 42.9 ppm.

IR (neat) $\nu$ 2950, 1727, 1597, 1492, 1287, 1215, 1047, 995, 921, 784, 697 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{21}$H$_{21}$O$_3$BrNa, 423.0566; found: 423.0565.
Methyl 2-(4-(allyloxy)-3-(trifluoromethyl)phenyl)-2-phenylpent-4-enoate (6ia)
Purified by flash column chromatography (elucent: petroleum ether/ethyl acetate = 20:1), colorless oil (63.3 mg, 65% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 2.4\) Hz, 1H), 7.36–7.20 (m, 6H), 6.89 (d, \(J = 8.8\) Hz, 1H), 6.07–5.97 (m, 1H), 5.62–5.51 (m, 1H), 5.46 (dd, \(J = 16.8, 0.8\) Hz, 1H), 5.28 (dd, \(J = 16.8, 0.8\) Hz, 1H), 4.97–4.92 (m, 2H), 4.61 (d, \(J = 4.8\) Hz, 2H), 3.69 (s, 3H), 3.20–3.08 (m, 2H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.3, 155.3 (d, \(J = 1.7\) Hz), 142.2, 134.4, 134.2, 133.8, 132.4, 128.7, 128.2, 127.7 (q, \(J = 5.5\) Hz), 127.2, 123.7 (q, \(J = 271.0\) Hz), 118.9, 118.2 (q, \(J = 30.5\) Hz), 117.6, 112.6, 69.3, 59.7, 52.6, 42.9 ppm.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.2 ppm.

IR (neat) \(\nu\) 2952, 1730, 1617, 1503, 1423, 1324, 1219, 1124, 1056, 994, 920, 699 cm\(^{-1}\).

HRMS-ESI (m/z): [M + Na]\(^+\) calcd for C\(_{22}\)H\(_{21}\)O\(_3\)F\(_3\)Na, 413.1335; found: 413.1336.

Methyl 2-(3-acetyl-4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6ja)
Purified by flash column chromatography (elucent: petroleum ether/ethyl acetate = 10:1), green oil (65.6 mg, 72% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 2.8\) Hz, 1H), 7.34–7.18 (m, 6H), 6.87 (d, \(J = 8.8\) Hz, 1H), 6.14–6.00 (m, 1H), 5.65–5.51 (m, 1H), 5.43 (dd, \(J = 17.2, 0.8\) Hz, 1H), 5.32 (dd, \(J = 10.4, 0.8\) Hz, 1H), 4.98–4.90 (m, 2H), 4.62 (d, \(J = 5.6\) Hz, 2H), 3.69 (s, 3H), 3.21–3.11 (m, 2H), 2.62 (s, 3H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.5, 174.4, 156.9, 142.4, 134.83, 134.81, 134.0, 132.6, 130.6, 128.7, 128.0, 127.5, 127.0, 118.6, 118.3, 112.3, 69.5, 59.6, 52.5, 42.7, 32.1 ppm.

IR (neat) \(\nu\) 2950, 1729, 1674, 1603, 1493, 1405, 1357, 1218, 992, 919, 817, 700 cm\(^{-1}\).

HRMS-ESI (m/z): [M + H]\(^+\) calcd for C\(_{23}\)H\(_{25}\)O\(_4\), 365.1747; found: 365.1748.
**Methyl 2-(4-(allyloxy)-3-cyanophenyl)-2-phenylpent-4-enoate (6ka)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 5:1), brown oil (79.6 mg, 92% yield).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 2.0$ Hz, 1H), 7.40–7.37 (m, 1H), 7.34–7.26 (m, 3H), 7.23–7.20 (m, 2H), 6.87 (d, $J = 8.8$ Hz, 1H), 6.10–5.96 (m, 1H), 5.62–5.50 (m, 1H), 5.47 (dd, $J = 17.2$, 1.2 Hz, 1H), 5.32 (dd, $J = 10.4$, 1.2 Hz, 1H), 5.00–4.90 (m, 2H), 4.64 (d, $J = 4.8$ Hz, 2H), 3.70 (s, 3H), 3.21–3.16 (m, 1H), 3.08–3.02 (m, 1H) ppm.

**13C NMR** (100 MHz, CDCl$_3$) $\delta$ 173.8, 159.0, 141.8, 135.5, 135.3, 134.4, 133.4, 131.9, 128.4, 127.4, 119.1, 118.4, 116.5, 111.9, 101.5, 69.6, 59.4, 52.7, 42.7 ppm.

**IR** (neat) $\nu$ 2951, 2226, 1728, 1606, 1497, 1447, 1268, 1209, 1127, 992, 921, 819, 699 cm$^{-1}$.

**HRMS-ESI** (m/z): [M + Na]$^+$ calcd for C$_{22}$H$_{21}$O$_3$NNa, 370.1414; found: 370.1415.

**Methyl 2-(allyloxy)-5-(1-methoxy-1-oxo-2-phenylpent-4-en-2-yl)benzoate (6la)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), green oil (78.3 mg, 82% yield).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 2.4$ Hz, 1H), 7.35–7.18 (m, 6H), 6.88 (d, $J = 9.2$ Hz, 1H), 6.12–5.98 (m, 1H), 5.64–5.54 (m, 1H), 5.50 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.29 ($J = 10.8$, 1.6 Hz, 1H), 4.98–4.89 (m, 2H), 4.64–4.57 (m, 2H), 3.85 (s, 3H), 3.69 (s, 3H), 3.15 (d, $J = 6.8$ Hz, 2H) ppm.

**13C NMR** (100 MHz, CDCl$_3$) $\delta$ 174.3, 166.7, 156.9, 142.3, 134.4, 134.3, 133.9, 132.7, 132.0, 128.7, 128.0, 127.0, 119.7, 118.6, 117.4, 113.0, 69.4, 59.5, 52.5, 52.0, 42.8 ppm.

**IR** (neat) $\nu$ 2951, 1726, 1606, 1495, 1435, 1216, 1082, 993, 920, 818, 786, 699 cm$^{-1}$.

**HRMS-ESI** (m/z): [M + H]$^+$ calcd for C$_{23}$H$_{25}$O$_5$, 381.1697; found: 381.1697.
Methyl 2-(4-(allyloxy)-3,5-dimethylphenyl)-2-phenylpent-4-enoate (6ma)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (61.0 mg, 70% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.16 (m, 5H), 6.90 (s, 2H), 6.18–6.00 (m, 1H), 5.65–5.51 (m, 1H), 5.42 (d, $J$ = 17.2 Hz, 1H), 5.24 (d, $J$ = 10.4 Hz, 1H), 5.00–4.81 (m, 2H), 4.30 (d, $J$ = 4.4 Hz, 2H), 3.68 (s, 3H), 3.18–3.15 (m, 1H), 3.09–3.04 (m, 1H), 2.23 (s, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.8, 154.9, 142.8, 137.6, 134.5, 134.3, 130.3, 129.3, 129.1, 127.8, 126.8, 118.1, 117.0, 73.1, 59.9, 52.4, 43.0, 16.7 ppm.

IR (neat) $\nu$ 2918, 1729, 1483, 1445, 1210, 1146, 988, 917, 790, 730, 699 cm$^{-1}$.

HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{23}$H$_{27}$O$_3$, 351.1955; found: 351.1957.

Methyl 2-(4-(allyloxy)-2-methylphenyl)-2-phenylpent-4-enoate (6na)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (51.8 mg, 62% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45–7.39 (m, 2H), 7.28–7.18 (m, 4H), 6.78–6.64 (m, 2H), 6.12–5.99 (m, 1H), 5.66–5.54 (m, 1H), 5.41 (dd, $J$ = 17.2, 1.2 Hz, 1H), 5.28 (dd, $J$ = 10.4, 1.2 Hz, 1H), 5.03–4.91 (m, 2H), 4.54–4.48 (m, 2H), 3.65 (s, 3H), 3.29–3.23 (m, 1H), 3.08–3.02 (m, 1H), 1.89 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.8, 157.4, 142.4, 139.1, 134.4, 133.5, 129.5, 128.9, 127.9, 126.7, 118.6, 118.0, 117.7, 110.9, 68.8, 58.7, 52.3, 43.6, 21.3 ppm (one $sp^2$ C-atom missing due to overlap).

IR (neat) $\nu$ 2948, 1729, 1483, 1445, 1210, 1146, 988, 917, 790, 730, 699 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{22}$H$_{24}$O$_3$Na, 359.1618; found: 359.1618.
Methyl 2-(4-(allyloxy)-2-fluorophenyl)-2-phenylpent-4-enolate (6oa)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (46.9 mg, 55% yield).

\[ ^{1} \text{H NMR} \] (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.47 (d, \( J = 7.6 \) Hz, 2H), 7.35–7.22 (m, 3H), 7.08–7.05 (m, 1H), 5.70–5.55 (m, 1H), 5.39 (dd, \( J = 17.2, 1.6 \) Hz, 1H), 5.28 (dd, \( J = 10.4, 1.6 \) Hz, 1H), 5.01–4.87 (m, 2H), 4.48 (d, \( J = 5.2 \) Hz, 2H), 3.67 (s, 3H), 3.28–3.15 (m, 2H).

\[ ^{13} \text{C NMR} \] (100 MHz, CDCl\textsubscript{3}) \( \delta \) 174.2, 157.4, 142.8, 137.4, 134.7, 134.5, 133.4, 130.2, 129.4, 127.8, 127.6, 126.0, 118.1, 117.7, 113.9, 68.8, 59.6, 52.3, 43.0, 21.7 ppm.

\[ ^{19} \text{F NMR} \] (376 MHz, CDCl\textsubscript{3}) \( \delta \) -107.5 (m, 1F) ppm.

\[ \text{IR} \] (neat) \( \nu \) 2950, 1732, 1622, 1503, 1431, 1220, 1161, 1125, 998, 919, 834, 698 cm\textsuperscript{-1}.

\[ \text{HRMS-ESI} \] (m/z): [M + H]\(^{+}\) calcld for C\textsubscript{22}H\textsubscript{22}O\textsubscript{3}F, 341.1547; found: 341.1548.

Methyl 2-(4-(allyloxy)phenyl)-2-(m-tolyl)pent-4-enolate (6ab)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (67.3 mg, 80% yield).

\[ ^{1} \text{H NMR} \] (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.21–7.13 (m, 3H), 7.07–7.00 (m, 3H), 6.83 (d, \( J = 8.4 \) Hz, 2H), 6.11–5.97 (m, 1H), 5.66–5.51 (m, 1H), 5.40 (d, \( J = 17.6 \) Hz, 1H), 5.26 (d, \( J = 10.4 \) Hz, 1H), 4.99–4.88 (m, 2H), 4.50 (d, \( J = 5.2 \) Hz, 2H), 3.67 (s, 3H), 3.18–3.07 (m, 2H), 2.30 (s, 3H) ppm.

\[ ^{13} \text{C NMR} \] (100 MHz, CDCl\textsubscript{3}) \( \delta \) 174.8, 157.4, 142.8, 137.4, 134.7, 134.5, 133.4, 130.2, 129.4, 127.8, 127.6, 126.0, 118.1, 117.7, 113.9, 68.8, 59.6, 52.3, 43.0, 21.7 ppm.

\[ \text{IR} \] (neat) \( \nu \) 2949, 1728, 1606, 1509, 1433, 1215, 1182, 995, 917, 828, 766, 700, 537 cm\textsuperscript{-1}.
**HRMS-ESI** (m/z): [M + Na]\(^+\) calcd for C\(_{22}\)H\(_{24}\)O\(_3\)Na, 359.1618; found: 359.1619.

Methyl 2-(4-(allyloxy)phenyl)-2-(3-methoxyphenyl)pent-4-enoate (6ac)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil (69.8 mg, 79% yield).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.23–7.14 (m, 3H), 6.87–6.74 (m, 5H), 6.11–5.97 (m, 1H), 5.66–5.52 (m, 1H), 5.40 (d, \(J = 17.2\) Hz, 1H), 5.27 (d, \(J = 10.4\) Hz, 1H), 4.99–4.90 (m, 2H), 4.51 (d, \(J = 4.8\) Hz, 2H), 3.73 (s, 3H), 3.67 (s, 3H), 3.12 (d, \(J = 6.8\) Hz, 2H) ppm.

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 174.6, 159.2, 157.4, 144.5, 134.5, 134.4, 133.4, 130.1, 128.8, 121.4, 118.2, 117.7, 115.4, 114.0, 111.7, 68.8, 59.7, 55.2, 52.4, 42.9 ppm.

**IR** (neat) \(\nu\) 2945, 1728, 1606, 1509, 1431, 1214, 996, 918, 733, 696, 530 cm\(^{-1}\).

**HRMS-ESI** (m/z): [M + Na]\(^+\) calcd for C\(_{22}\)H\(_{24}\)O\(_4\)Na, 375.1567; found: 375.1568.

Methyl 2-(4-(allyloxy)phenyl)-2-(3-fluorophenyl)pent-4-enoate (6ad)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil (69.4 mg, 82% yield).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.25–7.14 (m, 3H), 7.00 (d, \(J = 8.0\) Hz, 1H), 6.98–6.89 (m, 2H), 6.85 (d, \(J = 8.8\) Hz, 2H), 6.11–5.98 (m, 1H), 5.64–5.50 (m, 1H), 5.41 (d, \(J = 17.6\) Hz, 1H), 5.28 (d, \(J = 10.4\) Hz, 1H), 4.96–4.91 (m, 2H), 4.52 (d, \(J = 5.2\) Hz, 2H), 3.69 (s, 3H), 3.20–3.03 (m, 2H) ppm.

**\(^{13}\)C NMR** (101 MHz, CDCl\(_3\)) \(\delta\) 174.2, 162.4 (d, \(J = 243.4\) Hz), 157.6, 145.6 (d, \(J = 7.0\) Hz), 134.1, 134.0, 133.3, 129.9, 129.2 (d, \(J = 8.2\) Hz), 124.7 (d, \(J = 2.9\) Hz), 118.6, 117.8, 116.3 (d, \(J = 22.8\) Hz), 114.2, 113.8 (d, \(J = 21.0\) Hz), 68.9, 59.6, 52.5, 42.9 ppm.
**19F NMR** (376 MHz, CDCl₃) δ -113.2 (m, 1F ppm).

**IR** (neat) ν 2950, 1729, 1587, 1509, 1435, 1216, 1183, 995, 919, 826, 771, 692, 523 cm⁻¹.

**HRMS-ESI** (m/z): [M + Na]⁺ calcd for C₂₂H₂₁O₃F₃Na, 413.1335; found: 413.1336.

**Methyl 2-(4-(allyloxy)phenyl)-2-(3-(trifluoromethyl)phenyl)pent-4-enoate (6ae)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), yellow oil (68.0 mg, 70% yield).

**¹H NMR** (400 MHz, CDCl₃) δ 7.53–7.48 (m, 2H), 7.43–7.36 (m, 2H), 7.18 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.12–6.00 (m, 1H), 5.64–5.51 (m, 1H), 5.42 (dd, J = 17.2, 0.8 Hz, 1H), 5.29 (dd, J = 17.2, 0.8 Hz, 1H), 5.00–4.88 (m, 2H), 4.54 (d, J = 5.2 Hz, 2H), 3.71 (s, 3H), 3.24–3.19 (m, 1H), 3.11–3.06 (m, 1H) ppm.

**¹³C NMR** (100 MHz, CDCl₃) δ 174.2, 157.8, 144.0, 133.9, 133.7, 133.3, 132.8, 130.2 (q, J = 32.1 Hz), 129.9, 128.3, 125.8 (q, J = 3.7 Hz), 124.3 (q, J = 270.6 Hz), 123.8 (q, J = 3.8 Hz), 119.0, 117.9, 114.4, 68.9, 59.8, 52.6, 42.9 ppm.

**¹⁹F NMR** (376 MHz, CDCl₃): δ -62.5 ppm.

**IR** (neat) ν 2952, 1730, 1608, 1510, 1328, 1220, 1162, 1121, 1077, 996, 919, 830, 702 cm⁻¹.

**HRMS-ESI** (m/z): [M + Na]⁺ calcd for C₂₂H₂₁O₃F₃Na, 413.1335; found: 413.1336.

**Methyl 2-(4-(allyloxy)phenyl)-2-(3-cyanophenyl)pent-4-enoate (6af)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (65.9 mg, 76% yield).

**¹H NMR** (400 MHz, CDCl₃) δ 7.54–7.47 (m, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.11–5.98 (m, 1H), 5.61–5.48 (m, 1H), 5.41 (dd, J = 17.6, 1.2 Hz, 1H), 5.28 (dd, J = 10.4, 0.8 Hz, 1H), 4.96 (d, J = 10.4 Hz, 1H), 4.90 (d,
$J = 16.8 \text{ Hz, 1H)}, 4.53 \text{ (d, } J = 5.2 \text{ Hz, 2H)}, 3.70 \text{ (s, 3H)}, 3.24–3.19 \text{ (m, 1H)}, 3.03–2.98 \text{ (m, 1H) ppm.}$

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.7, 157.9, 144.6, 133.7, 133.4, 133.3, 133.2, 132.8, 130.4, 129.6, 128.5, 119.2, 119.0, 117.8, 114.5, 111.9, 68.8, 59.5, 52.7, 42.7 ppm.

IR (neat) ν 2951, 2229, 1728, 1607, 1509, 1214, 1182, 995, 920, 833, 692 cm$^{-1}$.

HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{22}$H$_{22}$O$_3$N, 348.1594; found: 348.1594.

Methyl 2-(4-(allyloxy)phenyl)-2-(4-(benzyloxy)phenyl)pent-4-enoate (6ag)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (93.0 mg, 87% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44–7.26 (m, 5H), 7.17–7.14 (m, 4H), 6.88 (d, $J = 8.8$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 6.09–5.96 (m, 1H), 5.67–5.50 (m, 1H), 5.39 (dd, $J = 17.2$, 1.2 Hz, 1H), 5.25 (dd, $J = 10.4$, 1.6 Hz, 1H), 5.01 (s, 2H), 4.97–4.89 (m, 2H), 4.49 (d, $J = 5.2$ Hz, 2H), 3.65 (s, 3H), 3.10 (d, $J = 6.8$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.9, 157.6, 157.3, 137.0, 135.1, 135.0, 134.5, 133.3, 130.04, 129.99, 128.6, 128.0, 127.6, 118.2, 117.7, 114.1, 114.0, 70.0, 68.8, 59.0, 52.3, 43.0 ppm.

IR (neat) ν 2948, 1726, 1606, 1507, 1219, 1178, 996, 917, 826, 734, 696 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{28}$H$_{28}$O$_4$Na, 451.1880; found: 451.1883.

Methyl 2-(4-(allyloxy)phenyl)-2-(4-fluorophenyl)pent-4-enoate (6ah)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil (75.6 mg, 89% yield).
\[ ^1H\text{ NMR (400 MHz, CDCl}_3\] \(\delta 7.23–7.10\) (m, 4H), \(6.95\) (t, \(J = 8.4\) Hz, 2H), \(6.85\) (d, \(J = 8.8\) Hz, 2H), \(6.12–5.94\) (m, 1H), \(5.64–5.49\) (m, 1H), \(5.41\) (d, \(J = 17.2\) Hz, 1H), \(5.27\) (d, \(J = 10.4\) Hz, 1H), \(4.98–4.85\) (m, 2H), \(4.52\) (d, \(J = 4.8\) Hz, 2H), \(3.68\) (s, 3H), \(3.19–3.01\) (m, 2H) ppm.

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\] \(\delta 174.6, 161.1\) (d, \(J = 244.6\) Hz), \(157.5, 138.6\) (d, \(J = 3.4\) Hz), \(134.5, 134.1, 133.3, 130.7\) (d, \(J = 7.9\) Hz), \(129.9, 118.5, 117.8, 114.6\) (d, \(J = 21.2\) Hz), \(114.2, 68.8, 59.2, 52.5, 43.0\) ppm.

\[ ^{19}\text{F NMR (376 MHz, CDCl}_3\] \(\delta -116.0\) (m, 1F) ppm.

\[ \text{IR (neat) } \nu 2950, 1728, 1606, 1507, 1434, 1219, 1182, 995, 919, 827, 554 \text{ cm}^{-1}.\]

\[ \text{HRMS-ESI (m/z): } [M + Na]^+ \text{ calcd for C}_{21}\text{H}_{21}\text{O}_3\text{FNa}, 363.1367; \text{found: 363.1368.}\]

\[ \text{Methyl 2-(4-(allyloxy)phenyl)-2-(4-bromophenyl)pent-4-enoate (6ai)} \]

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), yellow oil (67.4 mg, 67% yield).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\] \(\delta 7.41\) (d, \(J = 8.4\) Hz, 2H), \(7.17\) (d, \(J = 8.4\) Hz, 2H), \(7.11\) (d, \(J = 8.4\) Hz, 2H), \(6.86\) (d, \(J = 8.8\) Hz, 2H), \(6.12–5.99\) (m, 1H), \(5.64–5.50\) (m, 1H), \(5.42\) (d, \(J = 17.2\) Hz, 1H), \(5.29\) (d, \(J = 10.4\) Hz, 1H), \(4.99–4.89\) (m, 2H), \(4.56–4.49\) (m, 2H), \(3.69\) (s, 3H), \(3.18–3.04\) (m, 2H) ppm.

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\] \(\delta 174.3, 157.6, 142.0, 134.2, 133.9, 133.3, 130.93, 130.87, 129.9, 120.9, 118.7, 117.8, 114.2, 68.9, 59.4, 52.5, 42.8\) ppm.

\[ \text{IR (neat) } \nu 2949, 1729, 1607, 1509, 1218, 1182, 1008, 919, 821, 776, 533 \text{ cm}^{-1}.\]

\[ \text{HRMS-ESI (m/z): } [M + Na]^+ \text{ calcd for C}_{21}\text{H}_{21}\text{O}_3\text{BrNa}, 423.0566; \text{found: 423.0569.}\]

\[ \text{Methyl 2-(4-(allyloxy)phenyl)-2-(4-cyanophenyl)pent-4-enoate (6aj)} \]
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 3:1), yellow oil (44.6 mg, 51% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J$ = 8.0 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 2H), 7.17 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H), 6.14–5.96 (m, 1H), 5.64–5.47 (m, 1H), 5.41 (d, $J$ = 17.2 Hz, 1H), 5.29 (d, $J$ = 10.4 Hz, 1H), 4.99–4.85 (m, 2H), 4.53 (d, $J$ = 5.2 Hz, 2H), 3.70 (s, 3H), 3.25–3.20 (m, 1H), 3.05–3.00 (m, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.3, 159.5, 150.1, 135.98, 135.96, 134.8, 133.1, 131.6, 131.4, 120.8, 120.4, 119.5, 116.1, 112.3, 70.5, 61.6, 54.3, 44.3 ppm.

IR (neat) $\nu$ 2951, 2228, 1729, 1607, 1508, 1220, 1183, 995, 921, 827, 561 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{22}$H$_{21}$O$_3$NNa, 370.1414; found: 370.1416.

**Methyl 2-(4-(allyloxy)phenyl)-2-(3,5-difluorophenyl)pent-4-enoate (6ak)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (60.1 mg, 67% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H), 6.76 (d, $J$ = 7.6 Hz, 2H), 6.69 (t, $J$ = 8.4 Hz, 1H), 6.14–5.98 (m, 1H), 5.64–5.49 (m, 1H), 5.42 (d, $J$ = 17.2 Hz, 1H), 5.30 (d, $J$ = 10.8 Hz, 1H), 5.03–4.89 (m, 2H), 4.54 (d, $J$ = 5.2 Hz, 2H), 3.71 (s, 3H), 3.19–3.13 (m, 1H), 3.05–3.05 (m, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.8, 162.5 (dd, $J$ = 245.8, 12.6 Hz), 157.9, 147.1 (t, $J$ = 8.8 Hz), 133.6, 133.5, 133.3, 129.8, 119.0, 117.9, 114.4, 112.3 (dd, $J$ = 19.1, 7.0 Hz), 102.5 (t, $J$ = 25.2 Hz), 68.9, 59.7, 52.7, 42.8 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -110.2 (t, $J$ = 8.3 Hz, 2F) ppm.

IR (neat) $\nu$ 2952, 1731, 1596, 1509, 1432, 1215, 1183, 1116, 990, 920, 836, 512 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{21}$H$_{20}$O$_3$F$_2$Na, 381.1273; found: 381.1271.
Methyl 2-(4-(allyloxy)phenyl)-2-(benzo[d][1,3]dioxol-5-yl)pent-4-enolate (4al)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (71.6 mg, 78% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 6.74–6.73 (m, 3H), 6.11–6.01 (m, 1H), 5.93 (s, 2H), 5.65–5.54 (m, 1H), 5.42 (dd, $J = 17.6$, 1.6 Hz, 1H), 5.28 (dd, $J = 10.4$, 1.2 Hz, 1H), 4.98–4.94 (m, 2H), 4.53–4.52 (m, 2H), 3.69 (s, 3H), 3.10 (d, $J = 6.8$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.7, 157.4, 147.3, 146.3, 136.8, 134.8, 134.4, 133.4, 130.0, 122.1, 118.2, 117.7, 114.0, 109.8, 107.5, 101.1, 68.8, 59.4, 52.4, 43.1 ppm.

IR (neat) $\nu$ 2949, 2888, 1727, 1606, 1508, 1486, 1323, 1180, 1037, 922, 810, 774, 557 cm$^{-1}$.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for C$_{22}$H$_{22}$O$_5$Na, 389.1359; found: 389.1361.



Methyl 2-(4-(allyloxy)phenyl)-2-(naphthalen-2-yl)pent-4-enenate (6am)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (76.1 mg, 82% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80–7.74 (m, 3H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.43 (dd, $J = 6.4$, 3.2 Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 6.10–5.96 (m, 1H), 5.70–5.55 (m, 1H), 5.39 (d, $J = 17.2$ Hz, 1H), 5.26 (d, $J = 10.4$ Hz, 1H), 5.01–4.87 (m, 2H), 4.50 (d, $J = 5.2$ Hz, 2H), 3.69 (s, 3H), 3.25 (d, $J = 6.8$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.7, 157.5, 140.2, 134.6, 134.4, 133.4, 132.9, 132.3, 130.2, 128.3, 127.54, 127.48, 127.4, 127.3, 126.2, 126.1, 118.4, 117.8, 114.1, 68.8, 59.8, 52.5, 42.9 ppm.

IR (neat) $\nu$ 2949, 1727, 1606, 1508, 1217, 1182, 995, 917, 816, 745, 554, 476 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{25}$H$_{24}$O$_5$Na, 395.1618; found: 395.1619.
Methyl 2-(4-(allyloxy)phenyl)-2-(thiophen-3-yl)pent-4-enoate (6an)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil (68.9 mg, 84% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26–7.20 (m, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.97–6.92 (m, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 6.12–6.00 (m, 1H), 5.70–5.57 (m, 1H), 5.42 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.29 (dd, $J = 10.8$, 1.6 Hz, 1H), 5.04–4.95 (m, 2H), 4.53 (d, $J = 5.2$ Hz, 2H), 3.71 (s, 3H), 3.21–3.05 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.3, 157.5, 143.0, 134.8, 134.3, 133.3, 129.1, 129.0, 124.7, 123.2, 118.2, 117.8, 114.2, 68.8, 57.2, 52.4, 43.3 ppm.

IR (neat) $\nu$ 2949, 1728, 1607, 1508, 1433, 1210, 1181, 995, 918, 828, 786, 681 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{19}$H$_{20}$O$_3$NaS, 351.1025; found: 351.1027.

Isopropyl 2-(4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6ao)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil (67.1 mg, 77% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.19 (m, 7H), 6.83 (d, $J = 8.4$ Hz, 2H), 6.10–5.98 (m, 1H), 5.65–5.53 (m, 1H), 5.40 (dd, $J = 17.2$, 1.2 Hz, 1H), 5.26 (dd, $J = 10.4$, 1.2 Hz, 1H), 5.07–5.00 (m, 1H), 4.94–4.90 (m, 2H), 4.51 (d, $J = 5.2$ Hz, 2H), 3.18–3.06 (m, 2H), 1.13 (t, $J = 6.0$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.5, 157.3, 143.5, 134.9, 134.5, 133.4, 130.2, 129.0, 127.5, 126.7, 118.1, 117.7, 113.9, 68.8, 68.6, 59.6, 42.9, 21.5 ppm.

IR (neat) $\nu$ 2979, 1721, 1608, 1509, 1222, 1180, 1103, 992, 915, 826, 699 cm$^{-1}$.

HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{23}$H$_{27}$O$_3$, 351.1955; found: 351.1953.
Adamantan-2-yl 2-(4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6ap)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (57.9 mg, 52% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.18 (m, 7H), 6.83 (d, $J = 8.8$ Hz, 2H), 6.11–5.98 (m, 1H), 5.69–5.55 (m, 1H), 5.40 (d, $J = 17.6$ Hz, 1H), 5.27 (d, $J = 10.4$ Hz, 1H), 5.00–4.87 (m, 3H), 4.55–4.48 (m, 2H), 3.22–3.10 (m, 2H), 1.87 (brs, 2H), 1.79–1.73 (m, 5H), 1.69–1.59 (m, 5H), 1.40–1.37 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.5, 157.3, 143.2, 135.1, 134.6, 133.4, 130.3, 129.1, 127.7, 126.7, 118.0, 117.7, 113.9, 77.8, 68.8, 59.9, 42.9, 37.4, 36.3, 31.83, 31.81, 31.7, 27.2, 27.1 ppm (two $sp^3$ C-atom missing due to overlap).

IR (neat) $\nu$ 2905, 2854, 1719, 1509, 1449, 1225, 1180, 1100, 982, 916, 819, 698 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{30}$H$_{34}$O$_3$Na, 465.2400; found: 465.2404.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 2-(4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6aq)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil (74.0 mg, 66% yield), the dr value was determined by HPLC analysis to be 50:50.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.15 (m, 7H), 6.86–6.80 (m, 2H), 6.12–5.95 (m, 1H), 5.69–5.55 (m, 1H), 5.40 (d, $J = 17.2$ Hz, 1H), 5.27 (d, $J = 10.4$ Hz, 1H), 4.92–4.88 (m, 2H), 4.67–4.62 (m, 1H), 4.53–4.50 (m, 2H), 3.20–3.06 (m, 2H), 2.00–1.95 (m, 1H), 1.64–1.56 (m, 2H), 1.46–1.39 (m, 1H), 1.28–1.20 (m, 2H), 1.00–0.75 (m, 6H), 0.65 (t, $J = 6.4$ Hz, 3H), 0.49 (t, $J = 6.4$ Hz, 3H) ppm.
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.7, 157.41, 157.35, 143.0, 142.9, 135.0, 134.7, 134.5, 133.5, 133.4, 130.5, 130.1, 129.3, 128.9, 127.8, 127.6, 126.7, 126.6, 118.1, 117.7, 114.0, 113.8, 75.23, 75.17, 68.9, 59.78, 59.76, 47.1, 43.0, 42.9, 40.5, 34.3, 31.5, 25.4, 25.3, 22.91, 22.87, 22.2, 20.9, 15.7, 15.6 ppm.

IR (neat) ν 2953, 1719, 1608, 1509, 1447, 1218, 1178, 992, 915, 829, 699 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcld for C$_{30}$H$_{38}$O$_3$Na, 469.2713; found: 469.2716.

HPLC: CHIRALPAK ID-3, hexane/i-PrOH = 60/40, flow rate: 0.7 mL/min, $\lambda = 240$ nm, $t_{R1} = 4.093$ min, $t_{R2} = 5.127$ min, $dr = 50:50$.

(S)-3,7-Dimethyloct-6-en-1-yl 2-(4-(allyloxy)phenyl)-2-phenylpent-4-enoate (6ar)
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), colorless oil, (83.7 mg, 75% yield), the dr value was determined by HPLC analysis to be 52:48.

**1H NMR** (400 MHz, CDCl₃) δ 7.30–7.15 (m, 7H), 6.83 (d, J = 8.4 Hz, 2H), 6.11–5.97 (m, 1H), 5.66–5.51 (m, 1H), 5.40 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.03 (t, J = 7.2 Hz, 1H), 4.91 (d, J = 13.2 Hz, 2H), 4.51 (d, J = 4.8 Hz, 2H), 4.18–4.08 (m, 2H), 3.20–3.05 (m, 2H), 2.00–1.78 (m, 2H), 1.66 (s, 3H), 1.62–1.49 (m, 4H), 1.44–1.16 (m, 3H), 1.15–0.99 (m, 1H), 0.79 (d, J = 5.6 Hz, 3H) ppm.

**13C NMR** (100 MHz, CDCl₃) δ 174.2, 157.4, 143.0, 134.8, 134.5, 133.4, 131.3, 130.2, 129.0, 127.8, 126.7, 124.7, 118.1, 117.7, 113.9, 68.8, 63.6, 59.7, 42.9, 37.0, 35.4, 29.4, 25.8, 25.5, 19.3, 17.7 ppm.

**IR** (neat) ν 2914, 1725, 1608, 1509, 1446, 1212, 1180, 995, 917, 829, 699 cm⁻¹.

**HRMS-ESI** (m/z): [M + Na]⁺ calcd for C₃₀H₃₈O₃Na, 469.2713; found: 469.2718.

**HPLC**: CHIRALPAK ID-3, hexane, flow rate: 0.7 mL/min, λ = 240 nm, t_R1 = 14.273 min, t_R2 = 15.447 min, dr = 52:48.
Methyl 2-(4-(allyloxy)phenyl)-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)pent-4-enoate (6as)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 3:1), colorless oil (101.9 mg, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21 (s, 1H), 7.86 (d, $J = 7.2$ Hz, 1H), 7.56–7.38 (m, 2H), 7.37–7.22 (m, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 1H), 6.84 (d, $J = 7.6$ Hz, 2H), 6.10–5.92 (m, 1H), 5.69–5.49 (m, 1H), 5.40 (d, $J = 16.8$ Hz, 1H), 5.26 (d, $J = 10.4$ Hz, 1H), 5.15 (s, 2H), 5.02–4.88 (m, 2H), 4.50 (s, 2H), 3.70 (s, 3H), 3.18 (d, $J = 6.4$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.8, 174.4, 160.1, 157.4, 140.5, 136.8, 136.6, 135.4, 134.4, 134.0, 133.2, 132.7, 131.4, 129.8, 129.5, 129.2, 127.8, 124.3, 120.2, 118.6, 117.7, 114.1, 73.5, 68.7, 59.1, 52.4, 42.8 ppm.

IR (neat) $\nu$ 2949, 1727, 1645, 1605, 1509, 1485, 1297, 1218, 1013, 916, 828, 760, 638 cm$^{-1}$.

HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{29}$H$_{27}$O$_5$, 455.1853; found: 455.1851.
5. Investigation on the Asymmetric Synthesis

Preliminary attempt on the asymmetric version of this transformation has been carried out. However, rather poor stereoselectivity was achieved currently using the chiral disphosphine ligands with [Rh$_2$(OPiv)$_4$] or by employing chiral Rh(II) precursors with Xantphos (Scheme S1).

Scheme S1. Preliminary attempt on the asymmetric reactions of 1a, 2a and 3$^a$

$^a$Conditions: unless otherwise noted, 1a (0.375 mmol, 1.5 eq.), 2a (0.25 mmol, 1.0 eq.), 3 (0.75 mmol, 3.0 eq.), MeCN (2.0 mL), [Rh$_2$] complex (1.0 mol%), L (1.5 mol%), Cs$_2$CO$_3$ (3.5 eq.), 60 °C, 6.0 h. GC-yields. $er$ values were determined by HPLC analysis on a Chiralpak AD-H column.

6. Gram-Scale Experiment and Synthetic Applications

6.1 Gram-scale Synthesis of 6aa
In a glove box, to an oven-dried 100 mL flask equipped with a stir bar were added Rh$_2$(OPiv)$_4$ (30.5 mg, 5 x 10$^{-2}$ mmol, 1.0 mol%), Xantphos (43.4 mg, 7.5 x 10$^{-2}$ mmol, 1.5 mol%), Cs$_2$CO$_3$ (5.7 g, 17.5 mmol, 3.5 eq), phenol 1a (705 mg, 7.5 mmol, 1.5 eq.) and anhydrous CH$_3$CN (40 mL) under dry nitrogen atmosphere. Then, allyl ethyl carbonate 3 (1.95 g, 15 mmol, 3.0 eq.) and methyl 2-diazo-2-phenylacetate 2a (880 mg, 5.0 mmol, 1.0 eq.) were introduced by syringe. The resulting mixture was stirred at 60 °C for 12 h. Then the mixture was filtered, and the clear filtrate was collected. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 as the eluent) to give the desired product 6aa as a yellow oil (1.37 g, 85% yield).

6.2 Synthetic Applications

According to the literature methods$^{15}$: to a stirred solution of 6aa (64.4 mg, 0.2 mmol) in MeOH (2.0 mL) was added catalytic amounts of Pd(PPh$_3$)$_4$ (4.6 mg, 0.004 mmol; 2.0 mol%) under a nitrogen atmosphere. The slightly yellow solution was stirred for 5 min, then K$_2$CO$_3$ (82.8 mg, 0.6 mmol) was added. The resulting mixture was stirred at room temperature for 2.0 h. Then the resulting mixture was concentrated in vacuo, and the residue was treated with 2 N HCl. The aqueous solution was extracted with CH$_2$Cl$_2$. The organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound 7.

Methyl 2-(4-hydroxyphenyl)-2-phenylpent-4-enoate (7)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 4:1), yellow oil, (55.4 mg, 98% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31–7.17 (m, 5H), 7.11 (d, $J = 8.8$ Hz, 2H), 6.72 (d, $J = 8.4$ Hz, 2H), 6.03 (br, 1H), 5.64–5.50 (m, 1H), 4.97–4.88 (m, 2H), 3.68 (s, 3H), 3.19–3.06 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.4, 154.7, 142.8, 134.3, 134.2, 130.3, 128.9, 127.9, 126.9, 118.4, 114.9, 59.8, 52.6, 42.9 ppm.

IR (neat) $\nu$ 3391, 2950, 1705, 1612, 1512, 1434, 1361, 1434, 1361, 1279, 830, 699, 529 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{18}$H$_{18}$O$_3$Na, 305.1148; found: 305.1150.
According to the literature methods\textsuperscript{16}: to a solution of 7 (56.4 mg, 0.2 mmol), Et\textsubscript{3}N (30.3 mg, 0.3 mmol) and DMAP (2.4 mg, 0.02 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (2.0 M) was added Tf\textsubscript{2}O (84.6 mg, 0.3 mmol) at 0 °C. The resulting mixture was warmed to room temperature and stirred for another 1.0 h. The reaction was quenched with aqueous saturated NaHCO\textsubscript{3} and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure after filtration. The crude product was purified by flash column chromatography on silica gel to provide the pure compound 8a.

**Methyl 2-phenyl-2-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)pent-4-enoate (8a)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), yellow oil, (74.9 mg, 90% yield).

\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.32–7.24 (m, 7H), 7.20–7.17 (m, 2H), 5.64–5.49 (m, 1H), 5.00–4.87 (m, 2H), 3.70 (s, 3H), 3.24–3.19 (m, 1H), 3.11–3.06 (m, 1H) ppm.

\textbf{13C NMR} (100 MHz, CDCl\textsubscript{3}) $\delta$ 173.9, 148.3, 143.3, 141.9, 133.6, 131.2, 128.7, 128.4, 127.5, 120.6, 119.1, 118.9 (q, $J$ = 318.9 Hz), 60.1, 52.7, 42.9 ppm.

\textbf{19F NMR} (376 MHz, CDCl\textsubscript{3}) $\delta$ -73.0 (s, 1F) ppm.

\textbf{IR} (neat) $\nu$ 2953, 1731, 1499, 1422, 1206, 1137, 1016, 883, 836, 699, 606 cm\textsuperscript{-1}.

\textbf{HRMS-ESI} (m/z): [M + Na]\textsuperscript{+} calcd for C\textsubscript{19}H\textsubscript{17}O\textsubscript{5}F\textsubscript{3}NaS, 437.0641; found: 437.0643.

According to the literature methods\textsuperscript{17}: the mixture of 8a (82.8 mg, 0.2 mmol), PhB(OH)\textsubscript{2} (36.6 mg, 0.3 mmol), K\textsubscript{3}PO\textsubscript{4} (63.6 mg, 0.3 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (23.1 mg, 0.02 mmol) in 1,4-dioxane (4.0 mL) was heated at 110 °C for 8.0 h. The reaction was cooled to room temperature and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and filtered. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound 8b.
Methyl 2-((1,1'-biphenyl)-4-yl)-2-phenylpent-4-enoate (8b)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colourless oil (52.8 mg, 77% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 7.2$ Hz, 2H), 7.57 (d, $J = 7.2$ Hz, 2H), 7.46 (t, $J = 7.2$ Hz, 2H), 7.43–7.27 (m, 8H), 5.79–5.54 (m, 1H), 5.10–4.96 (m, 2H), 3.75 (s, 3H), 3.34–3.20 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.6, 142.6, 141.6, 140.6, 139.7, 134.3, 129.5, 129.0, 128.9, 128.0, 127.4, 127.1, 127.0, 126.6, 118.5, 60.2, 52.5, 42.9 ppm.

IR (neat) $\nu$ 2949, 1728, 1599, 1486, 1445, 1215, 1007, 913, 834, 760, 731, 696 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{24}$H$_{22}$O$_2$Na, 365.1512; found: 365.1515.

According to the literature methods$^{18}$: the mixture of 8a (82.8 mg, 0.2 mmol), trimethylsilylacetylene (39.2 mg, 0.4 mmol), CuI (5.7 mg, 0.03 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (14.0 mg, 0.02 mmol), NEt$_3$ (80.8 mg, 0.8 mmol) in DMF (1.5 mL) was heated to 90 °C for 6.0 h. The resulting mixture was cooled to room temperature and water (10 mL) was added. Then the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and filtered. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound 8c.

**Methyl 2-phenyl-2-(4-((trimethylsilyl)ethynyl)phenyl)pent-4-enoate (8c)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 20:1), yellow oil (63.2 mg, 87% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J = 8.0$ Hz, 2H), 7.36–7.14 (m, 7H), 5.68–5.47 (m, 1H), 5.03–4.83 (m, 2H), 3.69 (s, 3H), 3.24–3.06 (m, 2H), 0.26 (s, 9H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.2, 143.1, 142.2, 133.9, 131.5, 129.0, 128.9, 128.1, 127.1, 121.7, 118.7, 104.9, 94.6, 60.4, 52.5, 42.7, 0.1 ppm.

IR (neat) $\nu$ 2954, 2156, 1732, 1499, 1446, 1249, 1219, 1018, 840, 758, 698, 543 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{23}$H$_{26}$O$_2$NaSi, 385.1594; found: 385.1595.
According to the literature methods\textsuperscript{16}: the mixture of compound \textit{8a} (82.8 mg, 0.2 mmol), AcOK (39.2 mg, 0.4 mmol), Pd(dppf)Cl\textsubscript{2} (14.6 mg, 0.02 mmol) and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) in 1,4-dioxane (4.0 mL) was stirred in a sealed tube at 120 °C for 6.0 h. Then the reaction was cooled to room temperature and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and filtered. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound \textit{8d}.

**Methyl 2-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-4-enoate (8d)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (65.3 mg, 83% yield).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.74 (d, \(J = 7.6\) Hz, 2H), 7.32–7.19 (m, 7H), 5.65–5.50 (m, 1H), 4.97–4.88 (m, 2H), 3.68 (s, 3H), 3.17 (d, \(J = 7.2\) Hz, 2H), 1.33 (s, 12H) ppm.

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 174.4, 145.7, 142.4, 134.4, 134.2, 129.1, 128.5, 128.0, 127.0, 118.4, 83.9, 60.6, 52.5, 42.8, 25.0 ppm (one \(sp^2\) C-atom missing due to overlap).

\textbf{IR (neat)} \(\nu\) 2978, 1731, 1610, 1399, 1359, 1215, 1143, 1091, 1020, 858, 699, 658 cm\textsuperscript{-1}.

\textbf{HRMS-ESI (m/z):} [M + Na]\textsuperscript{+} calcd for C\textsubscript{24}H\textsubscript{29}O\textsubscript{4}BNa, 414.2087; found: 414.2092.

According to the literature methods\textsuperscript{19}: To a stirred solution of \textit{6aa} (64.4 g, 0.2 mmol) in hexane (1.0 mL) was added Et\textsubscript{2}AlCl (1 M in toluene; 0.4 mL, 0.4 mmol) at room temperature under nitrogen. The reaction was stirred at 80 °C for 6.0 h. Then the reaction mixture was cooled to 0 °C, followed by careful addition of HCl aq. (2 M; 0.8 mL). The aqueous phase was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and filtered. After
removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound 9.

**Methyl 2-(3-allyl-4-hydroxyphenyl)-2-phenylpent-4-enoate (9)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (62.0 mg, 96% yield).

**1H NMR (400 MHz, CDCl₃)** δ 7.31–7.19 (m, 5H), 7.06–6.96 (m, 2H), 6.70 (d, J = 8.4 Hz, 1H), 6.04–5.90 (m, 1H), 5.65–5.52 (m, 1H), 5.35 (br, 1H), 5.14–5.05 (m, 2H), 4.97–4.88 (m, 2H), 3.69 (s, 3H), 3.35 (d, J = 6.4 Hz, 2H), 3.20–3.05 (m, 2H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 175.1, 153.1, 142.9, 136.5, 134.45, 134.45, 131.1, 129.0, 128.5, 127.9, 126.8, 124.8, 118.2, 116.4, 115.3, 59.8, 52.5, 43.0, 35.2 ppm.

**IR (neat)** ν 3424, 2950, 1706, 1607, 1504, 1433, 1219, 1119, 995, 913, 699 cm⁻¹.

**HRMS-ESI (m/z):** [M + Na]⁺ calcd for C₂₁H₂₂O₃Na, 345.1461; found: 345.1463.

According to the literature methods²⁰: the mixture of compound 9 (80.5 mg, 0.25 mmol), Cu(OAc)₂ (136.5 mg, 0.75 mmol), PdCl₂ (2.2 mg, 0.0125 mmol) in DMF (1 mL) was stirred at 100 °C for 3.0 h. The resulting mixture was cooled to room temperature and water (10 mL) was added. Then the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄ and filtered. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound 10.

**Methyl 2-(2-methylbenzofuran-5-yl)-2-phenylpent-4-enoate (10)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil, (59.7 mg, 75% yield).

**1H NMR (400 MHz, CDCl₃)** δ 7.39 (s, 1H), 7.34–7.17 (m, 6H), 7.09 (d, J = 8.4 Hz, 1H), 6.30 (s, 1H), 5.67–5.53 (m, 1H), 4.99–4.86 (m, 2H), 3.68 (s, 3H), 3.30–3.11 (m, 2H), 2.42 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 174.9, 156.0, 153.7, 143.2, 136.9, 134.5, 129.1, 128.9, 127.9, 126.8, 124.5, 120.5, 118.2, 110.0, 102.9, 60.3, 52.4, 43.3, 14.2 ppm.
IR (neat) ν 2949, 1727, 1601, 1470, 1217, 1125, 997, 916, 785, 754, 699 cm⁻¹.

HRMS-ESI (m/z): [M + Na]⁺ calcd for C₂₁H₂₀O₃Na, 343.1305; found: 343.1306.

According to the literature methods²¹: the mixture of compound 7 (50.8 mg, 0.18 mmol), methyl acrylate (31.0 mg, 0.36 mmol), 2nd Grubbs catalyst (7.6 mg, 0.009 mmol) in DCM (1.0 mL) was stirred at 40 °C for 12.0 h. The resulting mixture was cooled to room temperature and the solvent was removed under reduced pressure. Then the crude product was purified by flash column chromatography on silica gel to provide the pure compound 11.

Dimethyl (E)-5-(4-hydroxyphenyl)-5-phenylhex-2-enedioate (11)

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 2:1), white solid, (46.7 mg, 76% yield), M.P. 155~156 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.30–7.26 (m, 2H), 7.25–7.20 (m, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.84–6.66 (m, 3H), 6.16 (s, 1H), 5.71 (d, J = 15.6 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.34–3.17 (m, 2H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 174.7, 167.2, 155.2, 145.8, 142.1, 133.2, 130.1, 128.7, 128.2, 127.3, 123.7, 115.1, 59.6, 52.8, 51.8, 41.4 ppm.

IR (neat) ν 3368, 2951, 1718, 1515, 1437, 1274, 1086, 968, 842, 727, 703, 614 cm⁻¹.

HRMS-ESI (m/z): [M + Na]⁺ calcd for C₂₀H₂₀O₅Na, 363.1203; found: 363.1201.

7. Mechanism Studies

7.1 The Preparation of 5aa’ and 5aa

According to the literature methods¹⁶: In a dried glass tube, the mixture of (2,4-²Bu₂C₆H₃O)₃PAuCl (52.7 mg, 0.06 mmol, 5.0 mol%), AgSbF₆ (20.6 mg, 0.06 mmol, 5.0 mol%) in CH₂Cl₂ (12 mL) was stirred at room temperature for 15 mins. Phenol 1a (169.2 mg, 1.8 mmol) was added to the reaction mixture at room temperature. Then a solution of methyl 2-diazo-2-phenylacetate 2a
(211.2 mg, 1.2 mmol) in 3.0 mL of CH$_2$Cl$_2$ was introduced into the reaction mixture by a syringe in 5 mins. The resulting mixture was continually stirred at room temperature for 10 min. The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product 5aa'.

**Methyl 2-(4-hydroxyphenyl)-2-phenylacetate (5aa')**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 3:1), yellow oil, (261.6 mg, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.20 (m, 5H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.71 (d, $J = 8.4$ Hz, 2H), 6.09 (br, 1H), 4.97 (s, 1H), 3.72 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.0, 155.2, 138.8, 130.4, 129.9, 128.7, 128.6, 127.4, 115.7, 56.3, 52.6 ppm.

In a dried glass flask, compound 5aa' (261.6 mg, 1.08 mmol), 3-bromopropene (196.0 mg, 1.62 mmol) and K$_2$CO$_3$ (149.0 mg, 1.08 mmol) in MeCN (3.0 mL) were stirred at 60 $^\circ$C for 1.0 h. The resulting mixture was cooled to room temperature and filtered. After removing the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel to provide the pure compound 5aa.

**Methyl 2-(4-(allyloxy)phenyl)-2-phenylacetate (5aa)**

Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), colorless oil (250.1 mg, 82% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36–7.16 (m, 7H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.10–5.94 (m, 1H), 5.39 (d, $J = 17.2$ Hz, 1H), 5.27 (d, $J = 10.8$ Hz, 1H), 4.98 (s, 1H), 4.50 (d, $J = 4.0$ Hz, 2H), 3.73 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.3, 157.9, 139.0, 133.3, 131.0, 129.8, 128.7, 128.6, 127.3, 117.8, 114.9, 68.9, 56.3, 52.4 ppm.

IR (neat) $\nu$ 2950, 1734, 1609, 1509, 1433, 1242, 1149, 996, 925, 823, 697, 526 cm$^{-1}$.

HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{18}$H$_{18}$O$_3$Na, 305.1148; found: 305.1148.
7.2 Controlled Experiments

Compound 5aa (70.5 mg, 0.25 mmol) and allyl ethyl carbonate 3 (97.5 mg, 0.75 mmol) were used as the substrates and the procedure was similar to the standard reaction procedure. After reacting for 6.0 h at 60 °C, 20 µL n-tridecane was added to the resulting mixture. Then filtering was conducted, and the filtrate was subjected to GC analysis to determine the GC yield of 6aa. All the results were summarized in Table S2.

**Table S2.** The reactions of 5aa with 3

| Entry | Variation from the standard reaction conditions | Yield of 6aa (%) |
|-------|-------------------------------------------------|------------------|
| 1     | none                                            | 99<sup>a</sup>   |
| 2     | no Rh<sub>2</sub>(OPiv)<sub>4</sub>              | 0<sup>b,c</sup>  |
| 3     | no Xantphos                                      | 7<sup>b</sup>    |
| 4     | no Cs<sub>2</sub>CO<sub>3</sub>                  | 0<sup>b,c</sup>  |
| 5     | only Rh<sub>2</sub>(OPiv)<sub>4</sub>, no Cs<sub>2</sub>CO<sub>3</sub>, no Xantphos | 0<sup>b,c</sup>  |
| 6     | only Xantphos, no Rh<sub>2</sub>(OPiv)<sub>4</sub>, no Cs<sub>2</sub>CO<sub>3</sub> | 0<sup>b,c</sup>  |
| 7     | only Cs<sub>2</sub>CO<sub>3</sub>, no Rh<sub>2</sub>(OPiv)<sub>4</sub>, no Xantphos | 0<sup>b,c</sup>  |
| 8     | none of Rh<sub>2</sub>(OPiv)<sub>4</sub>, Xantphos, Cs<sub>2</sub>CO<sub>3</sub> | 0<sup>b,c</sup>  |

<sup>a</sup>Isolated yield, <sup>b</sup>GC yield, <sup>c</sup>5aa remained unchanged.

The mixture of phenol 1a (35.3 mg, 0.375 mmol, 1.5 eq.) with diazo compound 2a (44.0 mg, 0.25 mmol, 1.0 eq.) was stirred for 3.0 h under the otherwise standard conditions, then allyl ethyl
carbonate 3 (97.5 mg, 0.75 mmol, 3.0 eq.) was subjected to this resulting mixture. After further stirring for another 3.0 h, 20 µL n-tridecane was added to the resulting mixture. Then filtering was conducted, and the filtrate was subjected to GC analysis to determine the GC yield of 6aa.

Diazo compound 2a (44.0 mg, 0.25 mmol) and allyl ethyl carbonate 3 (97.5 mg, 0.75 mmol) and allyl phenyl ether 4aa (50.3 mg, 0.375 mmol) were used as the substrates and the procedure was similar to the standard reaction procedure. After reacting for 6.0 h at 60 °C, no target reaction happened and 4aa was remained (detected by TLC and GC-MS analysis). Notably, neither the C-H insertion reaction or cyclopropanation reaction took place by GC-MS analysis (c-i). Additionally, the two-component reaction of 4aa and 2a afforded the similar results (c-ii). Instead, oxazole compound formed from the reaction of CH3CN (solvent) with diazo compound was detected by GC-MS in both two cases.

Diazo compound 5aa’ (60.5 mg, 0.25 mmol), allyl ethyl carbonate 3 (97.5 mg, 0.75 mmol) were used as the substrates and the procedure was similar to the standard reaction procedure. After cooling to ambient temperature, the mixture was filtered, and the clear filtrate was collected. After
removing the solvents in vacuo, the crude product was purified by flash column chromatography on silica gel to give the product 6aa (72.6 mg, 90% yield).

Compound 5aa (70.5 mg, 0.25 mmol) and deuterated allyl methyl carbonate (88.6 mg, 0.75 mmol) were used as the substrates and the procedure was similar to the standard reaction procedure. After reacting for 6.0 h at 60 °C, the mixture was filtered, and the clear filtrate was collected. After removing the solvents in vacuo, the crude product was purified by flash column chromatography on silica gel to give the product 6aa-D and 6aa-D’ in 75% yield (50:50 ratio determined by ¹H NMR analysis).

**Figure S2.** ¹H NMR spectrum comparison of 6aa with 6aa-D(D’) (400 MHz, CDCl₃)
2-Benzylphenol 1d (69.1 mg, 0.375 mmol), diazo compound 2a (44.0 mg, 0.25 mmol) and allyl phenyl ether 4aa (100.7 mg, 0.75 mmol) were used as the substrates and the procedure was similar to the standard reaction procedure. After stirring for 6.0 h at 60 °C, no 6da was detected by GC-MS analysis of the reaction mixture.

\[
\begin{align*}
\text{(f)} & \quad \text{Benzyl phenol} & \quad \text{Diazo} & \quad \text{Allyl phenyl ether} \\
& 1d & 2a & 4aa \\
\end{align*}
\]

\[
\begin{align*}
& \text{Standard conditions} \quad \Rightarrow \quad \text{GC-MS analysis} \\
& \text{No 6da detected} \\
\end{align*}
\]

\[
\begin{align*}
p-\text{methylphenol} \ 1p \ (40.6 \ mg, \ 0.375 \ mmol), \text{diazo compound} \ 2a \ (44.0 \ mg, \ 0.25 \ mmol) \text{and allyl ethyl carbonate} \ 3 \ (97.5 \ mg, \ 0.75 \ mmol) \text{were used as the substrates and the procedure was similar to the standard reaction procedure. After stirring for 6.0 h at 60 °C, no target product 6pa was detected by GC-MS analysis. Then 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) was added to the reaction mixture as the internal standard. After that, filtering was conducted and the filtrate was concentrated under vacuum. The residue obtained was directly subjected to }^{1}H\text{-NMR analysis and } O\text{-allylation product (4pa) was observed in 30% yield.}
\end{align*}
\]

\[
\begin{align*}
\text{(g)} & \quad \text{p-Methyl phenol} & \quad \text{Diazo} & \quad \text{Allyl ethyl carbonate} \\
& 1p & 2a & 3 \\
\end{align*}
\]

\[
\begin{align*}
& \text{Standard conditions} \quad \Rightarrow \quad \text{GC-MS analysis} \\
& \text{No 6pa observed} \\
\end{align*}
\]

\[
\begin{align*}
\text{Phenol} \ 1a \ (35.3 \ mg, \ 0.375 \ mmol) \text{and diazo compound} \ 2a \ (44.0 \ mg, \ 0.25 \ mmol) \text{were used as the substrates and the procedure was similar to the standard reaction procedure. After reacting for 6.0 h at 60 °C, 20 µL } n\text{-tridecane was added to the resulting mixture. Then filtering was conducted and the filtrate was subjected to GC analysis to determine the GC yield of 5aa’ and 12. All the results were summarized in Table S3.}
\end{align*}
\]

\[
\begin{align*}
\text{(h)} & \quad \text{Phenol} & \quad \text{Diazo} \\
& 1a & 2a \\
\end{align*}
\]

\[
\begin{align*}
& \text{Reaction conditions} \quad \Rightarrow \quad \text{GC analysis} \\
& \text{GC yield of 5aa’ and 12} \\
\end{align*}
\]

\textbf{Table S3.} The reactions of 1a with 2a
Table S4. The reactions of 1a with 2a

| Entry | Base     | Yield of 5aa’ (%) | Yield of 12 (%) |
|-------|----------|-------------------|-----------------|
| 1     | Cs₂CO₃   | 94                | 0               |
| 2     | K₂CO₃    | 26                | 0               |
| 3     | Na₂CO₃   | 5                 | 0               |
| 4     | Li₂CO₃   | 0                 | 1               |
| 5     | --       | 0                 | 0               |

Variation from the standard reaction conditions

| Entry | Variation from the standard reaction conditions | Yield of 5aa’ (%) | Yield of 12 (%) |
|-------|--------------------------------------------------|-------------------|-----------------|
| 1     | none                                             | 76<sup>a</sup>    | 0               |
| 2     | no Xantphos                                      | 78<sup>a</sup>    | 0               |
| 3     | no Cs₂CO₃                                        | trace             | trace           |

<sup>a</sup>Isolated yield.

Phenol 1a (23.5 mg, 0.25 mmol) and diazo compound 2a (52.8 mg, 0.30 mmol) were used as the substrates in the specific reaction conditions and the procedure was similar to the standard reaction procedure. After reacting for 6.0 h at 60 °C, 20 µL n-tridecane was added to the resulting mixture. Then filtering was conducted and the filtrate was subjected to GC analysis to determine the GC yield of 5aa’ and 12. All the results were summarized in Table S4.
8. Copies of NMR spectra

[Images of 1H NMR and 13C NMR spectra of 6aa]
$^1$H NMR (400 MHz, CDCl$_3$) of 6ba

$^1$C NMR (100 MHz, CDCl$_3$) of 6ba
**S41**

**H NMR (400 MHz, CDCl₃) of 6ca**

![H NMR spectrum of 6ca](image)

**C NMR (100 MHz, CDCl₃) of 6ca**

![C NMR spectrum of 6ca](image)
$^1$H NMR (400 MHz, CDCl$_3$) of 6da

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6da

S42
$^1$H NMR (400 MHz, CDCl$_3$) of 6ea

$^13$C NMR (100 MHz, CDCl$_3$) of 6ea
1H NMR (400 MHz, CDCl3) of 6fa

13C NMR (100 MHz, CDCl3) of 6fa
$^{1}H$ NMR (400 MHz, CDCl$_3$) of $6ga$

$^{13}C$ NMR (100 MHz, CDCl$_3$) of $6ga$
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 6ha

$^{13}C$ NMR (100 MHz, CDCl$_3$) of 6ha
$^{19}$F NMR (376 MHz, CDCl$_3$) of 6ia
$\text{H NMR (400 MHz, CDCl}_3\text{) of 6ja}$

$\text{C NMR (100 MHz, CDCl}_3\text{) of 6ja}$
$^{1}H$ NMR (400 MHz, CDCl$_3$) of $6ka$

$^{13}C$ NMR (100 MHz, CDCl$_3$) of $6ka$
$^1$H NMR (400 MHz, CDCl$_3$) of 6la

$^1$C NMR (100 MHz, CDCl$_3$) of 6la
$^1$H NMR (400 MHz, CDCl$_3$) of 6na

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6na
S54
$^{19}$F NMR (376 MHz, CDCl$_3$) of 60a
$^{1}$H NMR (400 MHz, CDCl$_3$) of 6ab

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6ab
S57
$^1$H NMR (400 MHz, CDCl$_3$) of 6ad

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6ad
$^{19}$F NMR (376 MHz, CDCl$_3$) of 6ad
$^1$H NMR (400 MHz, CDCl$_3$) of 6ae

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6ae
$^{19}$F NMR (376 MHz, CDCl$_3$) of 6ae
1H NMR (400 MHz, CDCl₃) of 6af

13C NMR (100 MHz, CDCl₃) of 6af
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 6ag

$^{13}C$ NMR (100 MHz, CDCl$_3$) of 6ag
$\text{H NMR (400 MHz, CDCl}_3\text{) of 6ah}$

$\text{C NMR (100 MHz, CDCl}_3\text{) of 6ah}$
$^{19}$F NMR (376 MHz, CDCl$_3$) of 6ah
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 6ai

$^{13}C$ NMR (100 MHz, CDCl$_3$) of 6ai
$^1$H NMR (400 MHz, CDCl$_3$) of $6a$j

$^{13}$C NMR (100 MHz, CDCl$_3$) of $6a$j
19F NMR (376 MHz, CDCl₃) of 6ak
S70
$^1$H NMR (400 MHz, CDCl$_3$) of 6am

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6am
S72
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 6ao

$^{13}C$ NMR (100 MHz, CDCl$_3$) of 6ao
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 6ap

$^{13}C$ NMR (100 MHz, CDCl$_3$) of 6ap
$^1$H NMR (400 MHz, CDCl$_3$) of 6aq

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6aq
$^1$H NMR (400 MHz, CDCl$_3$) of 6ar

$^1$C NMR (100 MHz, CDCl$_3$) of 6ar
$^1$H NMR (400 MHz, CDCl$_3$) of 6as

$^{13}$C NMR (100 MHz, CDCl$_3$) of 6as
$^1$H NMR (400 MHz, CDCl$_3$) of 7

$^{13}$C NMR (100 MHz, CDCl$_3$) of 7
$^{19}$F NMR (376 MHz, CDCl$_3$) of 8a
S81
$^1$H NMR (400 MHz, CDCl$_3$) of 8c

$^1$C NMR (100 MHz, CDCl$_3$) of 8c
$^1$H NMR (400 MHz, CDCl$_3$) of 8d

$^1$C NMR (100 MHz, CDCl$_3$) of 8d
S84

H NMR (400 MHz, CDCl₃) of 9

13C NMR (100 MHz, CDCl₃) of 9
$^1$H NMR (400 MHz, CDCl$_3$) of 10

$^1$C NMR (100 MHz, CDCl$_3$) of 10
$^1$H NMR (400 MHz, CDCl$_3$) of $^{13}$C NMR (100 MHz, CDCl$_3$) of 11
$\text{H NMR (400 MHz, CDCl}_3\text{) of 5aa'}$

$\text{13C NMR (100 MHz, CDCl}_3\text{) of 5aa'}$
$^{1}$H NMR (400 MHz, CDCl$_3$) of 5aa

$^{13}$C NMR (100 MHz, CDCl$_3$) of 5aa
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