Supporting Information

An intramolecular Heck reaction of enol ethers involving β-alkoxyl elimination followed by the β-hydride elimination process: access to (Z)-orthoformyl/keto-cinnamates†

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General Information
All reactions were performed under a N$_2$ atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ using a Bruker Avance 300 MHz NMR spectrometer (referenced internally to Me$_4$Si). Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (TMS) with the resonance of the nondeuterated solvent or TMS as the internal standard. $^1$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet), coupling constant (Hz), and integral. Data for $^{13}$C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using a Varian instrument with the ESI-MS technique.
Experimental Procedure

General procedure for the synthesis of substrates 1 and 3:

\[
\text{R}^1\text{H} + \text{R}^2\text{CO}_2\text{R}^4 \xrightarrow{\text{DABCO, 80 °C}} \text{R}^1\text{H} + \text{R}^2\text{CO}_2\text{R}^4
\]

To a mixture of alcohol (S1) (0.5 mmol) and allenoate or alkynoate (S2) (0.6 mmol) was added DABCO (2.8 mg). The reaction mixture was stirred at 80 °C until the substrate alcohol or allene was consumed (TLC monitored). The resulting mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 40:1) to give the desired product.¹

General procedure for the synthesis of (Z)-ortho-formyl-cinnamates 2 and (Z)-ortho-keto-cinnamates 4:

\[
\text{R}^1\text{H} + \text{R}^2\text{CO}_2\text{R}^4 \xrightarrow{\text{Pd(dba)}_2, \text{NaHCO}_3, n-\text{Bu}_4\text{NCl, DMF}} \text{R}^1\text{H} + \text{R}^2\text{CO}_2\text{R}^4
\]

An oven-dried Schlenk tube was charged with 1 or 3 (0.5 mmol), Pd(dba)_2 (14.4 mg, 0.025 mmol), NaHCO_3 (84 mg, 1.0 mmol), n-Bu_4NCl (139 mg, 0.5 mmol) and dry DMF (2 mL) under N_2. The mixture was stirred at 120 °C for 4 h. After the reaction was cooled, H_2O (10 mL) was added. The resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed sequentially with water and saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was loaded onto a silica gel column and separated chromatographically (petroleum ether/ethyl acetate, 20:1) to give the desired product.

Procedure for synthesis of compound 2a on 5 mmol scale:

An oven-dried Schlenk tube was charged with 1a (1.73 g, 5 mmol), Pd(dba)_2 (144 mg, 0.25 mmol), NaHCO_3 (840 mg, 10 mmol), n-Bu_4NCl (1.39 g, 5 mmol) and dry DMF (20 mL) under N_2. The mixture was stirred at 120 °C for 4 h. After the reaction was
cooled, H₂O (50 mL) was added. The resulting mixture was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed sequentially with water and saturated NaCl solution, dried over Na₂SO₄, filtered and concentrated under vacuum. The residue was loaded onto a silica gel column and separated chromatographically (petroleum ether/ethyl acetate, 20:1) to give the desired product 2a (828 mg, 76%).

**Procedure for synthesis of compound 5:**

\[
\begin{array}{c}
\text{CHO} \\
\text{EtO₂C} \\
\text{Me} \\
\end{array} \xrightarrow{\text{NH₂OH·HCl}} \begin{array}{c}
\text{Me} \\
\text{CO₂Et} \\
\end{array}
\]

NH₂OH·HCl (34.7 mg, 0.5 mmol) was added to a solution of 2a (109 mg, 0.5 mmol), Et₃N (101 mg, 1.0 mmol) in 5:1 THF:H₂O (5 mL) at room temperature. The reaction was stirred for 3 h. The H₂O layer was extracted with two portions of DCM, the combined organic layer dried (MgSO₄), and the solvent was removed under reduced pressure to afford the nitrone product 5 (102.5 mg, 88%) as a yellow oil without further purification.²

**Procedure for synthesis of compound 6:**

\[
\begin{array}{c}
\text{CHO} \\
\text{EtO₂C} \\
\text{Me} \\
\end{array} \xrightarrow{\text{NaBH₄}} \begin{array}{c}
\text{Me} \\
\text{O} \\
\end{array}
\]

2a (109 mg, 0.5 mmol) was added to a solution of NaBH₄ (152 mg, 4 mmol), CuCl (74 mg, 0.75 mmol) in MeOH (10 mL) at 0 °C. After stirred for 30 minutes, the reaction mixture was filtered and extracted with Et₂O. The extract was washed with water, dried (Na₂SO₄), and evaporated under vacuum. Flash chromatography of the residue on silica gel (petroleum ether/ethyl acetate, 20:1) gave product 6 (66.1 mg, 76%).³
Characterization Data

Ethyl (E)-3-((2-iodo-4-(trifluoromethyl)benzyl)oxy)but-2-enoate (1d)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.09 (s, 1H), 7.64 (d, $J$ = 8.1 Hz, 1H), 7.54 (d, $J$ = 8.1 Hz, 1H), 5.15 (s, 1H), 4.83 (s, 2H), 4.16 (q, $J$ = 7.2 Hz, 2H), 2.41 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 171.1, 167.5, 141.9, 136.1 (q, $J$ = 2.2 Hz), 131.7 (q, $J$ = 19.8 Hz), 128.5, 125.3 (q, $J$ = 2.1 Hz), 122.8 (q, $J$ = 162.6 Hz), 96.4, 92.9, 73.2, 59.6, 18.9, 14.4.

Ethyl (E)-3-((5-bromo-2-iodobenzyl)oxy)but-2-enoate (1f)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.68 (d, $J$ = 8.4 Hz, 1H), 7.54 (s, 1H), 7.17 (d, $J$ = 8.4 Hz, 1H), 5.14 (s, 1H), 4.75 (s, 2H), 4.23-4.12 (m, 2H), 2.40 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.2, 166.6, 139.5, 138.8, 131.8, 130.5, 121.8, 93.9, 91.7, 72.0, 58.6, 17.9, 13.4.

Ethyl (E)-3-((2-iodo-3,5-dimethylbenzyl)oxy)but-2-enoate (1l)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.05 (s, 1H), 7.03 (s, 1H), 5.17 (s, 1H), 4.82 (s, 2H), 4.16 (q, $J$ = 7.2 Hz, 2H), 2.45 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.8, 166.9, 141.2, 137.0, 136.9, 129.5, 126.1, 99.9, 91.2, 73.8, 58.4, 28.0, 19.8, 18.0, 13.4.

Ethyl (E)-3-((3-iodonaphthalen-2-yl)methoxy)but-2-enoate (1j)
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.41 (s, 1H), 7.86-7.81 (m, 2H), 7.76-7.71 (m, 1H), 7.53-7.50 (m, 2H), 5.23 (s, 1H), 4.95 (s, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 2.49 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.7, 166.8, 137.9, 133.4, 132.8, 131.5, 127.0, 126.9, 126.1, 125.9, 125.5, 93.3, 91.4, 72.8, 58.5, 18.0, 13.4.

Benzyl (E)-3-((2-iodobenzyl)oxy)but-2-enoate (1k)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 7.8$ Hz, 1H), 7.44-7.33 (m, 7H), 7.07-7.02 (m, 1H), 5.25 (s, 1H), 5.17 (s, 2H), 4.81 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 172.3, 167.6, 139.5, 137.7, 136.6, 129.9, 128.9, 128.6, 128.5, 128.3, 128.1, 97.8, 92.1, 73.9, 65.6, 19.1.

 tert-Butyl (E)-3-((2-iodobenzyl)oxy)but-2-enoate (1l)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 7.8$ Hz, 1H), 7.43-7.34 (m, 2H), 7.07-7.01 (m, 1H), 5.10 (s, 1H), 4.78 (s, 2H), 2.36 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.6, 166.3, 138.4, 137.0, 128.8, 128.0, 127.4, 96.8, 93.1, 78.4, 72.6, 27.4, 17.8.

Ethyl (E)-3-((2-fluorophenyl)(4-iodo-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate (3d)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 8.4$ Hz, 1H), 7.56-7.53 (m, 3H), 7.48-7.37 (m, 4H), 7.30 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.22-7.12 (m, 3H), 6.65 (s, 1H), 5.12 (s, 1H), 4.17-4.09 (m, 2H), 2.48 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.3, 167.7, 160.7 (d, $J = 247.8$ Hz), 141.7, 140.5, 140.4, 139.6, 130.6 (d, $J = 8.2$ Hz), 129.1 (d, $J = 4.4$ Hz), 129.0, 128.9, 128.0, 127.0, 126.9, 125.2 (d, $J = 13.4$ Hz), 124.4 (d, $J = 3.5$ Hz), 115.8 (d, $J = 21.2$ Hz), 97.4, 94.5, 78.7 (d, $J = 2.8$ Hz), 59.6,
(E)-3-((2-fluorophenyl)(4-iodo-3'-methyl-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate (3e)

1H NMR (300 MHz, CDCl3): δ 7.93 (d, J = 8.1 Hz, 1H), 7.36-7.30 (m, 1H), 7.25-7.22 (m, 3H), 7.20-7.08 (m, 5H), 7.03 (dd, J = 8.1, 2.1 Hz, 1H), 6.54 (s, 1H), 5.02 (s, 1H), 4.09 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ 170.4, 167.9, 160.7 (d, J = 247.6 Hz), 142.3, 140.4, 140.0, 139.9, 135.3, 131.1, 130.7, 130.6 (d, J = 8.2 Hz), 129.7, 129.6, 129.1 (d, J = 3.2 Hz), 127.9, 126.2, 125.3 (d, J = 13.4 Hz), 124.5 (d, J = 3.6 Hz), 115.9 (d, J = 21.2 Hz), 97.1, 94.6, 78.7 (d, J = 2.8 Hz), 59.7, 20.4, 19.1, 14.5.

Ethyl (E)-3-((2-fluorophenyl)(4-iodo-3'-methyl-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate (3f)

1H NMR (300 MHz, CDCl3): δ 7.81 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 7.22-7.14 (m, 5H), 7.08-7.01 (m, 4H), 6.48 (s, 1H), 4.95 (s, 1H), 4.02-3.95 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ 170.4, 167.8, 160.8 (d, J = 247.9 Hz), 141.9, 140.5, 140.4, 139.7, 138.7, 130.6 (d, J = 8.2 Hz), 129.1 (d, J = 3.2 Hz), 129.0, 128.9, 128.8, 127.8, 127.1, 125.2 (d, J = 13.5 Hz), 124.4 (d, J = 3.5 Hz), 124.2, 115.9 (d, J = 21.2 Hz), 97.3, 94.6, 78.8 (d, J = 2.8 Hz), 59.6, 21.6, 19.1, 14.4.
Ethyl

(E)-3-((2-fluorophenyl)(4-iodo-4'-methoxy-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate (3g)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 8.4$ Hz, 1H), 7.47-7.43 (m, 3H), 7.39-7.32 (m, 1H), 7.24 (dd, $J = 8.1$, 2.4 Hz, 1H), 7.19-7.09 (m, 3H), 6.99-6.94 (m, 2H), 6.56 (s, 1H), 5.04 (s, 1H), 4.09 (q, $J = 7.2$ Hz, 2H), 3.84 (s, 3H), 2.42 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.4, 167.9, 160.8 (d, $J = 247.8$ Hz), 159.7, 141.4, 140.5, 140.4, 132.2, 130.6 (d, $J = 8.2$ Hz), 129.2 (d, $J = 3.2$ Hz), 128.5, 128.1, 126.7, 125.3 (d, $J = 13.4$ Hz), 124.5 (d, $J = 3.4$ Hz), 115.9 (d, $J = 21.2$ Hz), 114.5, 96.6, 94.6, 78.8 (d, $J = 2.9$ Hz), 59.6, 55.5, 19.1, 14.5.

![Structure Image](attachment:structure_g.png)

Ethyl

(E)-3-((2-fluorophenyl)(4-iodo-2',4'-dimethyl-[1,1'-biphenyl]-3-yl)methoxy)but-2-enoate (3h)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 8.1$ Hz, 1H), 7.37-7.31 (m, 1H), 7.18-7.00 (m, 8H), 6.53 (s, 1H), 5.01 (s, 1H), 4.09 (q, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 2.14 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.3, 167.8, 160.6 (d, $J = 247.6$ Hz), 142.2, 139.8, 139.7, 137.6, 137.4, 135.0, 131.4, 131.0, 130.4 (d, $J = 8.2$ Hz), 129.6, 129.5, 128.9 (d, $J = 3.2$ Hz), 126.7, 125.2 (d, $J = 13.3$ Hz), 124.4 (d, $J = 3.4$ Hz), 115.8 (d, $J = 21.2$ Hz), 96.7, 94.4, 78.6 (d, $J = 2.8$ Hz), 59.5, 21.1, 20.2, 19.0, 14.4.

![Structure Image](attachment:structure_h.png)

Ethyl

(E)-3-((2'-chloro-4-iodo-[1,1'-biphenyl]-3-yl)(2-fluorophenyl)methoxy)but-2-enoate (3i)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.95 (d, $J = 8.1$ Hz, 1H), 7.47-7.44 (m, 1H), 7.37-7.30
(m, 5H), 7.16-7.09 (m, 4H), 6.56 (s, 1H), 5.02 (s, 1H), 4.09 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.4, 167.9, 160.8 (d, J = 247.6 Hz), 140.0, 139.9, 139.7, 139.0, 132.4, 131.2, 130.6 (d, J = 8.2 Hz), 130.3, 129.8, 129.3, 129.2, 127.2, 125.2 (d, J = 13.6 Hz), 124.5 (d, J = 3.4 Hz), 115.9 (d, J = 21.2 Hz), 98.0, 94.6, 78.5 (d, J = 2.9 Hz), 59.7, 19.2, 14.5.

![Chemical Structure](image)

Ethyl

$(E)$-3-(((3'-chloro-4-iodo-[1,1'-biphenyl]-3-yl)(2-fluorophenyl)methoxy)but-2-enoate (3j)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.93 (d, J = 8.4 Hz, 1H), 7.47-7.44 (m, 2H), 7.36-7.31 (m, 4H), 7.22 (dd, J = 8.4, 2.1 Hz, 1H), 7.16-7.08 (m, 3H), 6.57 (s, 1H), 5.04 (s, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.3, 167.8, 160.8 (d, J = 247.9 Hz), 141.6, 140.9, 140.6, 140.3, 135.0, 130.7 (d, J = 8.2 Hz), 130.3, 129.1 (d, J = 3.0 Hz), 128.8, 128.0, 127.1, 127.0, 125.2, 125.1 (d, J = 13.6 Hz), 124.5 (d, J = 3.6 Hz), 115.9 (d, J = 21.1 Hz), 98.2, 94.6, 78.8 (d, J = 2.7 Hz), 59.6, 19.1, 14.4.

![Chemical Structure](image)

Ethyl

$(E)$-3-(((2-fluorophenyl)(2-iodo-5-(naphthalen-2-yl)phenyl)methoxy)but-2-enoate (3I)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.00-7.97 (m, 2H), 7.91-7.85 (m, 3H), 7.66-7.62 (m, 2H), 7.53-7.50 (m, 2H), 7.43-7.36 (m, 2H), 7.22-7.12 (m, 3H), 6.63 (s, 1H), 5.09 (s, 1H), 4.15-4.08 (m, 2H), 2.46 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.3, 167.8, 160.8 (d, J = 247.9 Hz), 141.6, 140.9, 140.6, 140.3, 135.0, 130.7 (d, J = 8.2 Hz), 130.0, 129.1 (d, J = 3.0 Hz), 128.8, 128.1, 127.1, 127.0, 125.2, 125.1 (d, J = 13.6 Hz), 124.5 (d, J = 3.6 Hz), 115.9 (d, J = 21.1 Hz), 98.2, 94.6, 78.7 (d, J = 2.7 Hz), 59.6, 19.1, 14.5.
Ethyl (Z)-3-(2-formylphenyl)but-2-enoate (2a)

88.3 mg, 81% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.05 (s, 1H), 7.93 (dd, $J = 7.5, 1.2$ Hz, 1H), 7.59 (td, $J = 7.5, 1.2$ Hz, 1H), 7.49-7.44 (m, 1H), 7.14 (dd, $J = 7.5, 1.2$ Hz, 1H), 6.10 (s, 1H), 3.92 (q, $J = 7.2$ Hz, 2H), 2.22 (s, 3H), 1.02 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.4, 165.2, 153.5, 144.7, 133.9, 132.4, 129.3, 127.9, 127.7, 120.2, 60.1, 28.1, 14.0; HRMS (ESI): [M + H]$^+$ calcd for C$_{13}$H$_{15}$O$_3$: m/z 219.1016, found: 219.1014. The Z stereochemistry was confirmed by NOESY ($\delta$ 6.10 and 2.22).

Ethyl (Z)-3-(2-formyl-5-methylphenyl)but-2-enoate (2b)

91.6 mg, 79% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.99 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 6.94 (s, 1H), 6.08 (s, 1H), 3.93 (q, $J = 7.2$ Hz, 2H), 2.42 (s, 3H), 2.21 (s, 3H), 1.03 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.1, 165.3, 153.8, 144.9, 144.8, 130.2, 129.5, 128.8, 128.2, 119.9, 60.0, 28.1, 22.0, 14.0; HRMS (ESI): [M + H]$^+$ calcd for C$_{14}$H$_{17}$O$_3$*: m/z 233.1172, found: 233.1172. Spectral data were consistent with data reported in the literature.$^4$

Ethyl (Z)-3-(5-chloro-2-formylphenyl)but-2-enoate (2c)

94.5 mg, 75% yield; colorless oil; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 9.91 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.38 (s, 1H), 6.16 (s, 1H), 3.86 (q, $J = 7.2$ Hz, 2H), 2.20 (s, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$):
δ 190.6, 164.3, 152.2, 145.8, 138.6, 131.0, 130.5, 127.9, 127.6, 119.9, 59.5, 27.0, 13.8; HRMS (ESI): [M + H]^+ calcd for C_{13}H_{14}ClO_3^+: m/z 253.0626, found: 253.0621.

Ethyl (Z)-3-(2-formyl-5-(trifluoromethyl)phenyl)but-2-enoate (2d)

93.0 mg, 65% yield; colorless oil; ^1H NMR (300 MHz, CDCl₃): δ 10.09 (s, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.42 (s, 1H), 6.16 (q, J = 1.5 Hz, 1H), 3.97-3.89 (m, 2H), 2.25 (d, J = 1.5 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H); ^13C NMR (100 MHz, CDCl₃): δ 190.1, 164.8, 151.2, 145.0, 135.0 (q, J = 31.6 Hz), 129.9 (q, J = 207.0 Hz), 129.2, 124.8 (q, J = 2.9 Hz), 124.7, (q, J = 2.9 Hz), 122.3, 121.2, 60.2, 27.8, 13.7; HRMS (ESI): [M + H]^+ calcd for C_{14}H_{14}F₃O₃^+: m/z 287.0890, found: 287.0886.

Ethyl (Z)-3-(2-formyl-4-methylphenyl)but-2-enoate (2e)

96.3 mg, 83% yield; colorless oil; ^1H NMR (300 MHz, CDCl₃): δ 10.01 (s, 1H), 7.74 (s, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.09 (s, 1H), 3.94 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.07 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H); ^13C NMR (75 MHz, CDCl₃): δ 191.6, 165.3, 153.8, 141.9, 137.8, 134.8, 132.3, 129.6, 127.6, 120.1, 60.0, 28.3, 21.2, 14.1; HRMS (ESI): [M + H]^+ calcd for C_{14}H_{17}O₃^+: m/z 233.1172, found: 233.1170.

Ethyl (Z)-3-(4-bromo-2-formylphenyl)but-2-enoate (2f)

102.1 mg, 69% yield; colorless oil; ^1H NMR (300 MHz, CDCl₃): δ 9.96 (s, 1H), 8.05
(d, $J = 2.1$ Hz, 1H), 7.70 (dd, $J = 8.1$, 2.1 Hz, 1H), 7.04 (d, $J = 8.1$ Hz, 1H), 6.12 (q, $J = 1.5$ Hz, 1H), 3.95 (q, $J = 7.1$ Hz, 2H), 2.20 (d, $J = 1.5$ Hz, 3H), 1.07 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 189.8, 165.0, 152.0, 143.4, 136.7, 133.8, 131.7, 129.4, 122.1, 120.8, 60.3, 28.0, 14.0; HRMS (ESI): [M + Na]$^+$ calcd for C$_{13}$H$_{13}$BrNaO$_3$: $m/z$ 318.9940, found: 318.9939.

Ethyl (Z)-3-(2-formyl-6-methylphenyl)but-2-enoate (2g)
84.7 mg, 73% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.02 (s, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 6.17 (s, 1H), 3.92 (q, $J = 7.2$ Hz, 2H), 2.23 (s, 3H), 2.17 (s, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.9, 165.1, 153.0, 144.2, 135.8, 134.5, 131.9, 127.5, 127.2, 120.8, 60.0, 26.9, 18.7, 14.0; HRMS (ESI): [M + H]$^+$ calcd for C$_{14}$H$_{17}$O$_3$: $m/z$ 233.1172, found: 233.1172.

Ethyl (Z)-3-(6-formyl-2,3-dimethylphenyl)but-2-enoate (2h)
92.3 mg, 75% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.95 (s, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 6.18 (q, $J = 1.2$ Hz, 1H), 3.97-3.86 (m, 2H), 2.35 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 190.6, 164.0, 152.5, 143.0, 131.7, 128.9, 128.1, 125.9, 120.0, 58.8, 26.2, 20.1, 14.2, 12.8; HRMS (ESI): [M + H]$^+$ calcd for C$_{15}$H$_{19}$O$_3$: $m/z$ 247.1329, found: 247.1330.
Ethyl (Z)-3-(2-formyl-4,6-dimethylphenyl)but-2-enoate (2i)
83.6 mg, 68% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.98 (s, 1H), 7.57 (s, 1H), 7.28 (s, 1H), 6.16 (q, $J = 1.5$ Hz, 1H), 3.94 (q, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 2.19 (s, 3H), 2.15 (d, $J = 1.5$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 192.0, 165.2, 153.4, 141.5, 137.2, 136.8, 134.4, 131.9, 127.6, 120.7, 60.0, 27.1, 21.0, 18.6, 14.1; HRMS (ESI): [M + H]$^+$ calcd for C$_{15}$H$_{19}$O$_3$+: $m/z$ 247.1329, found: 247.1330.

Ethyl (Z)-3-(3-formylnaphthalen-2-yl)but-2-enoate (2j)
91.2 mg, 68% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.16 (s, 1H), 8.43 (s, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.64-7.55 (m, 3H), 6.13 (q, $J = 1.5$ Hz, 1H), 3.90 (q, $J = 7.2$ Hz, 2H), 2.29 (d, $J = 1.5$ Hz, 3H), 0.98 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 190.5, 164.4, 153.5, 137.8, 134.6, 132.5, 130.7, 130.2, 128.5, 128.2, 126.8, 125.9, 125.4, 118.4, 58.8, 26.9, 12.9; HRMS (ESI): [M + H]$^+$ calcd for C$_{17}$H$_{17}$O$_3$+: $m/z$ 269.1172, found: 269.1171.

Benzyl (Z)-3-(2-formylnaphthalen-2-yl)but-2-enoate (2k)
107.8 mg, 77% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.96 (s, 1H), 7.81 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.50 (td, $J = 7.5$, 1.2 Hz, 1H), 7.36 (td, $J = 7.5$, 0.9 Hz, 1H), 7.22-7.19 (m, 3H), 7.08-7.04 (m, 3H), 6.08 (q, $J = 1.2$ Hz, 1H), 4.85 (s, 2H), 2.15 (d, $J = 1.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 190.2, 163.8, 153.3, 143.2, 134.6, 132.8, 131.2, 128.5, 127.4, 127.2, 127.1, 126.8, 126.5, 118.5, 64.9, 27.0; HRMS (ESI): [M + H]$^+$ calcd for C$_{18}$H$_{17}$O$_3$+: $m/z$ 281.1172, found: 281.1174.
tert-Butyl (Z)-3-(2-formylphenyl)but-2-enoate (2l)

87.3 mg, 71% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.06 (s, 1H), 7.92 (dd, $J = 7.8$, 0.9 Hz, 1H), 7.58 (td, $J = 7.5$, 1.2 Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.14 (dd, $J = 7.8$, 0.9 Hz, 1H), 6.02 (q, $J = 1.5$ Hz, 1H), 2.18 (d, $J = 1.5$ Hz, 3H), 1.13 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 190.3, 163.6, 149.3, 144.3, 132.8, 131.2, 127.4, 167.2, 126.6, 121.6, 79.3, 27.0, 26.7; HRMS (ESI): [M + Na]$^+$ calcd for C$_{15}$H$_{18}$NaO$_3$: $m/z$ 269.1148, found: 269.1148.

Ethyl (Z)-3-(2-formylphenyl)pent-2-enoate (2m)

77.7 mg, 67% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.02 (s, 1H), 7.93 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.58 (td, $J = 7.5$, 1.5 Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.12 (dd, $J = 7.5$, 0.9 Hz, 1H), 6.07 (q, $J = 1.5$ Hz, 1H), 3.91 (q, $J = 7.2$ Hz, 2H), 2.52-2.43 (m, 2H), 1.11 (t, $J = 7.2$ Hz, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.3, 165.4, 158.3, 144.2, 133.6, 132.7, 128.7, 127.9, 118.5, 60.0, 34.1, 13.9, 11.7; HRMS (ESI): [M + H]$^+$ calcd for C$_{14}$H$_{17}$O$_3$: $m/z$ 233.1172, found: 233.1177.

Ethyl (Z)-3-(2-formylphenyl)-3-phenylacrylate (2n)

100.8 mg, 72% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.15 (s, 1H), 7.96 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.61-7.47 (m, 2H), 7.34-7.23 (m, 6H), 6.03 (s, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 1.18 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.2, 165.5, 152.7, 145.4, 138.8, 134.5, 133.7, 130.8, 129.4, 129.2, 129.1, 128.5, 128.2, 123.0,
60.7, 14.1; HRMS (ESI): [M + H]$^+$ calcd for $C_{18}H_{17}O_3^+$: $m/z$ 281.1172, found: 281.1170.

![Chemical Structure](image)

Ethyl (Z)-3-(2-formylphenyl)-3-(p-tolyl)acrylate (2o)

100.0 mg, 68% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.12 (s, 1H), 7.95 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.57 (td, $J = 7.5, 1.5$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.31 (dd, $J = 7.5, 0.9$ Hz, 1H), 7.14 (s, 4H), 5.99 (s, 1H), 4.15 (q, $J = 7.2$ Hz, 2H), 2.35 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 199.7, 165.8, 158.5, 142.1, 136.1, 131.9, 129.1, 127.8, 127.3, 116.4, 59.6, 28.4, 27.5, 14.1; HRMS (ESI): [M + H]$^+$ calcd for $C_{19}H_{19}O_3^+$: $m/z$ 295.1329, found: 295.1327.

![Chemical Structure](image)

Ethyl (Z)-3-(2-acetylphenyl)but-2-enoate (4a)

88.2 mg, 76% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.78 (dd, $J = 7.5, 0.9$ Hz, 1H), 7.49 (td, $J = 7.5, 1.5$ Hz, 1H), 7.39 (td, $J = 7.5, 1.5$ Hz, 1H), 7.06 (dd, $J = 7.5, 0.9$ Hz, 1H), 5.85 (s, 1H), 3.91 (q, $J = 7.2$ Hz, 2H), 2.56 (s, 3H), 2.20 (s, 3H), 1.05 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 199.7, 165.8, 158.5, 142.1, 136.1, 131.9, 129.1, 127.8, 127.3, 116.4, 59.6, 28.4, 27.5, 14.1; HRMS (ESI): [M + H]$^+$ calcd for $C_{14}H_{17}O_3^+$: $m/z$ 233.1172, found: 233.1173.

![Chemical Structure](image)

Ethyl (Z)-3-(2-benzoylphenyl)but-2-enoate (4b)

105.8 mg, 72% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.84-7.81 (m, 2H),
7.56-7.50 (m, 2H), 7.45-7.33 (m, 4H), 7.20 (d, J = 7.6 Hz, 1H), 5.79 (s, 1H), 3.87 (q, J = 7.2 Hz, 2H), 2.24 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 197.5, 165.4, 156.6, 142.1, 137.7, 137.0, 132.9, 130.9, 130.7, 129.6, 128.2, 127.6, 126.5, 118.1, 59.7, 28.1, 14.1; HRMS (ESI): [M + H]\(^+\) calcd for C\(_{19}\)H\(_{19}\)O\(_3\): m/z 295.1329, found: 295.1329.

[Chemical structure image]

Ethyl (Z)-3-(2-(4-methoxybenzoyl)phenyl)but-2-enoate (4c)

113.4 mg, 70% yield; colorless oil; \(^1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, J = 7.8 Hz, 1H), 7.52-7.47 (m, 1H), 7.42-7.32 (m, 2H), 7.20-7.17 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 5.78 (s, 1H), 3.90-3.83 (m, 5H), 2.22 (s, 2H), 1.01 (t, J = 7.2 Hz, 3H); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 196.3, 165.4, 163.6, 156.6, 141.6, 137.5, 133.1, 130.5, 130.4, 129.1, 127.6, 126.5, 118.2, 113.4, 59.7, 55.6, 28.2, 14.1; HRMS (ESI): [M + H]\(^+\) calcd for C\(_{20}\)H\(_{21}\)O\(_4\): m/z 325.1434, found: 325.1435.

[Chemical structure image]

Ethyl (Z)-3-(2-(4-methoxybenzoyl)phenyl)but-2-enoate (4c)

113.4 mg, 70% yield; colorless oil; \(^1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, J = 7.8 Hz, 1H), 7.52-7.47 (m, 1H), 7.42-7.32 (m, 2H), 7.20-7.17 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 5.78 (s, 1H), 3.90-3.83 (m, 5H), 2.22 (s, 2H), 1.01 (t, J = 7.2 Hz, 3H); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 196.3, 165.4, 163.6, 156.6, 141.6, 137.5, 133.1, 130.5, 130.4, 129.1, 127.6, 126.5, 118.2, 113.4, 59.7, 55.6, 28.2, 14.1; HRMS (ESI): [M + H]\(^+\) calcd for C\(_{20}\)H\(_{21}\)O\(_4\): m/z 325.1434, found: 325.1435.

[Chemical structure image]

Ethyl (Z)-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (4d)

133.9 mg, 69% yield; colorless oil; \(^1^H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.77 (dd, J = 8.1, 1.8 Hz, 1H), 7.71 (s, 1H), 7.65 (td, J = 7.5, 1.8 Hz, 1H), 7.58-7.51 (m, 1H), 7.47-7.36 (m, 3H), 7.28 (d, J = 7.8 Hz, 1H), 7.24-7.13 (m, 2H), 5.89 (q, J = 1.5 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 2.26 (d, J = 1.5 Hz, 3H), 1.10 (t, J = 7.2 Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 193.8, 165.5, 161.0 (d, J = 203.5 Hz), 156.3, 141.3, 140.0, 139.9, 137.2, 133.8 (d, J = 6.7 Hz), 132.2, 130.3, 129.0, 128.9, 128.4, 127.8, 127.3 (d, J = 7.4 Hz), 127.2, 124.0 (d, J = 2.9 Hz), 118.1, 116.5 (d, J = 17.0 Hz), 59.8, 27.7, 14.1; HRMS (ESI): [M + H]\(^+\) calcd for C\(_{25}\)H\(_{22}\)F\(_2\)O\(_3\): m/z 389.1547, found: 389.1545.
Ethyl (Z)-3-(3-(2-fluorobenzoyl)-2'-methyl-[1,1'-biphenyl]-4-yl)but-2-enolate (4e)

132.7 mg, 66% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.61 (td, $J = 7.5$, 1.8 Hz, 1H), 7.52-7.43 (m, 3H), 7.25-7.08 (m, 7H), 5.89 (q, $J = 1.5$ Hz, 1H), 3.97 (q, $J = 7.2$ Hz, 2H), 2.27 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 193.8, 165.7, 160.9 (d, $J = 253.8$ Hz), 156.5, 141.1, 140.6, 136.3, 135.5, 133.7 (d, $J = 8.5$ Hz), 132.5, 132.1 (d, $J = 2.1$ Hz), 131.3, 131.2, 130.6, 129.9, 127.9, 127.8, 127.3 (d, $J = 12.2$ Hz), 126.0, 124.0 (d, $J = 3.7$ Hz), 118.1, 116.5 (d, $J = 21.5$ Hz), 59.8, 27.8, 20.6, 14.1; HRMS (ESI): [M + H]$^+$ calcd for C$_{26}$H$_{24}$F$_3$O$_3$: m/z 403.1704, found: 403.1706. The Z stereochemistry was confirmed by NOESY (δ 5.89 and 2.27).

Ethyl (Z)-3-(3-(2-fluorobenzoyl)-3'-methyl-[1,1'-biphenyl]-4-yl)but-2-enolate (4f)

134.7 mg, 67% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.73 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.67 (s, 1H), 7.62 (td, $J = 7.5$, 1.8 Hz, 1H), 7.54-7.46 (m, 1H), 7.35-7.30 (m, 3H), 7.25-7.11 (m, 4H), 5.85 (q, $J = 1.2$ Hz, 1H), 3.96 (q, $J = 7.2$ Hz, 2H), 2.39 (s, 3H), 2.23 (d, $J = 1.2$ Hz, 3H), 1.07 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 193.9, 165.6, 161.1 (d, $J = 254.5$ Hz), 156.4, 141.2, 140.2, 140.0, 138.6, 137.2, 133.8 (d, $J = 8.6$ Hz), 132.3 (d, $J = 2.0$ Hz), 130.4, 129.0, 128.9, 128.6, 128.3, 128.1, 127.2 (d, $J = 11.8$ Hz), 124.4, 124.0 (d, $J = 3.8$ Hz), 118.1, 116.6 (d, $J = 21.5$ Hz), 59.8, 27.7, 21.6, 14.1; HRMS (ESI): [M + H]$^+$ calcd for C$_{26}$H$_{24}$FO$_3$: m/z 403.1704, found: 403.1703.
Ethyl (Z)-3-(3-(2-fluorobenzoyl)-4'-methoxy-[1,1'-biphenyl]-4-yl)but-2-enoate (4g) 131.7 mg, 63% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.71 (dd, $J$ = 7.8, 1.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.52-7.46 (m, 3H), 7.24-7.11 (m, 3H), 6.97-6.94 (m, 2H), 5.86 (q, $J$ = 1.5 Hz, 1H), 3.96 (q, $J$ = 7.2 Hz, 2H), 3.83 (s, 3H), 2.23 (d, $J$ = 1.5 Hz, 3H), 1.08 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 193.9, 165.6, 161.0 (d, $J$ = 254.5 Hz), 159.5, 156.5, 140.7, 139.7, 137.2, 133.7 (d, $J$ = 8.6 Hz), 132.4, 132.2 (d, $J$ = 2.0 Hz), 129.9, 128.9, 128.3, 128.2, 127.3 (d, $J$ = 11.9 Hz), 124.0 (d, $J$ = 3.7 Hz), 118.0, 116.6 (d, $J$ = 2.0 Hz), 114.4, 59.8, 55.4, 27.7, 14.1; HRMS (ESI): [M + H]$^+$ calcd for C$_{26}$H$_{24}$F$_2$O$_4$: m/z 419.1653, found: 419.1654. The Z stereochemistry was confirmed by NOESY (δ 5.86 and 2.23).

Ethyl (Z)-3-(3-(2-fluorobenzoyl)-2',4'-dimethyl-[1,1'-biphenyl]-4-yl)but-2-enoate (4h) 131.0 mg, 63% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.62 (td, $J$ = 7.5, 1.8 Hz, 1H), 7.51-7.43 (m, 3H), 7.24-7.04 (m, 6H), 5.90 (q, $J$ = 1.2 Hz, 1H), 3.98 (q, $J$ = 7.2 Hz, 2H), 2.35 (s, 3H), 2.28 (d, $J$ = 1.2 Hz, 3H), 2.25 (s, 3H), 1.08 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 193.8, 165.6, 160.9 (d, $J$ = 253.7 Hz), 159.5, 140.9, 140.5, 137.7, 137.5, 136.2, 135.3, 133.6 (d, $J$ = 8.6 Hz), 132.6, 132.0 (d, $J$ = 2.0 Hz), 131.4, 131.3, 129.8, 127.8, 127.3 (d, $J$ = 12.2 Hz), 126.7, 124.0 (d, $J$ = 3.7 Hz), 118.0, 116.4 (d, $J$ = 21.4 Hz), 59.7, 27.8, 21.1, 20.5, 14.1; HRMS (ESI): [M + H]$^+$ calcd for C$_{27}$H$_{36}$F$_2$O$_4$: m/z 417.1860, found: 417.1861. The Z stereochemistry was confirmed by NOESY (δ 5.90 and 2.28).
Ethyl (Z)-3-(2'-chloro-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (4i)

132.9 mg, 63% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.65-7.57 (m, 3H), 7.51-7.43 (m, 2H), 7.36-7.28 (m, 3H), 7.26-7.09 (m, 3H), 5.88 (q, $J = 1.5$ Hz, 1H), 3.96 (q, $J = 7.2$ Hz, 2H), 2.26 (d, $J = 1.5$ Hz, 3H), 1.06 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 193.6, 165.6, 161.0 (d, $J = 254.6$ Hz), 156.3, 141.9, 139.2, 138.0, 136.3, 133.8 (d, $J = 8.6$ Hz), 132.7, 132.6, 132.2 (d, $J = 2.0$ Hz), 131.6, 131.4, 130.2, 129.1, 127.8, 127.2 (d, $J = 12.0$ Hz), 127.1, 124.0 (d, $J = 3.7$ Hz), 118.2, 116.6 (d, $J = 21.4$ Hz), 59.8, 27.8, 14.1; HRMS (ESI): [M + H]$^+$ calcd for C$_{25}$H$_{21}$ClF$_3$O$: m/z$ 423.1158, found: 423.1161. The Z stereochemistry was confirmed by NOESY ($\delta$ 5.88 and 2.26).

Ethyl (Z)-3-(3'-chloro-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (4j)

141.4 mg, 67% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.72 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.54-7.50 (m, 2H), 7.43-7.33 (m, 3H), 7.26-7.12 (m, 3H), 5.86 (q, $J = 1.5$ Hz, 1H), 3.96 (q, $J = 7.2$ Hz, 2H), 2.23 (d, $J = 1.5$ Hz, 3H), 1.08 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 193.7, 165.5, 161.1 (d, $J = 254.6$ Hz), 156.1, 142.0, 141.8, 138.7, 137.5, 134.9, 134.0 (d, $J = 8.7$ Hz), 132.3 (d, $J = 1.8$ Hz), 130.3, 130.2, 128.8, 128.6, 127.9, 127.4, 127.0 (d, $J = 11.6$ Hz), 125.4, 124.1 (d, $J = 3.7$ Hz), 118.3, 116.7 (d, $J = 21.4$ Hz), 59.9, 27.7, 14.2; HRMS (ESI): [M + H]$^+$ calcd for C$_{25}$H$_{21}$ClF$_3$O$: m/z$ 423.1158, found: 423.1160. The Z stereochemistry was confirmed by NOESY ($\delta$ 5.86 and 2.26).
Ethyl (Z)-3-(4'-chloro-3-(2-fluorobenzoyl)-[1,1'-biphenyl]-4-yl)but-2-enoate (4k)

149.8 mg, 71% yield; colorless oil; 1H NMR (300 MHz, CDCl3): δ 7.71 (dd, J = 7.8, 1.8 Hz, 1H), 7.64 (s, 1H), 7.62 (td, J = 7.5, 1.8 Hz, 1H), 7.53-7.45 (m, 3H), 7.38 (d, J = 8.7 Hz, 2H), 7.26-7.11 (m, 3H), 5.86 (q, J = 1.5 Hz, 1H), 3.96 (q, J = 7.2 Hz, 2H), 2.23 (d, J = 1.5 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ 193.7, 165.5, 161.0 (d, J = 254.6 Hz), 156.2, 141.7, 138.8, 138.4, 137.4, 134.0, 133.9 (d, J = 8.5 Hz), 132.2 (d, J = 2.0 Hz), 130.1, 129.2, 128.7, 128.6, 128.5, 128.4, 124.0 (d, J = 3.8 Hz), 118.2, 116.6 (d, J = 21.5 Hz), 59.8, 27.7, 14.2; HRMS (ESI): [M + H]+ calcd for C25H21ClFO3+: m/z 423.1158, found: 423.1156.

Ethyl (Z)-3-(2-(2-fluorobenzoyl)-4-(naphthalen-2-yl)phenyl)but-2-enoate (4l)

133.6 mg, 61% yield; colorless oil; 1H NMR (300 MHz, CDCl3): δ 8.00 (d, J = 1.5 Hz, 1H), 7.91-7.84 (m, 4H), 7.82 (s, 1H), 7.70-7.63 (m, 2H), 7.53-7.48 (m, 3H), 7.30 (d, J = 7.8 Hz, 1H), 7.23-7.13 (m, 2H), 5.88 (q, J = 1.5 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 2.26 (d, J = 1.5 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ 193.9, 165.6, 161.1 (d, J = 254.6 Hz), 156.4, 141.4, 140.0, 137.4, 137.3, 133.9 (d, J = 8.6 Hz), 133.6, 132.8, 132.3 (d, J = 1.8 Hz), 130.6, 129.3, 128.7, 128.5, 128.3, 127.8, 127.2 (d, J = 11.8 Hz), 126.6, 126.3, 126.1, 125.4, 124.0 (d, J = 3.8 Hz), 118.2, 116.6 (d, J = 21.5 Hz), 59.9, 27.7, 14.2; HRMS (ESI): [M + H]+ calcd for C29H24FO3+: m/z 439.1704, found: 439.1704. The Z stereochemistry was confirmed by NOESY (δ 5.88 and 2.26).
1-(2-Ethoxy-2-oxoethyl)-1-methyl-1H-isoindole 2-oxide (5)

102.5 mg, 88% yield; yellow oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.70 (s, 1H), 7.38-7.32 (m, 4H), 3.99-3.88 (m, 2H), 3.02 (s, 2H), 1.61 (s, 3H), 1.02 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 168.6, 142.8, 133.3, 132.8, 128.9, 127.8, 121.6, 120.4, 60.7, 40.9, 29.8, 24.4, 14.0; HRMS (ESI): [M + H]$^+$ calcd for C$_{13}$H$_{16}$NO$_3$: m/z 234.1125, found: 234.1123.

5-Methylbenzo[c]oxepin-3(1H)-one (6)

66.1 mg, 76% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.53-7.51 (m, 2H), 7.44-7.42 (m, 2H), 6.33 (q, $J$ = 1.5 Hz, 1H), 5.02 (s, 2H), 2.36 (d, $J$ = 1.5 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 168.0, 147.8, 137.7, 134.8, 129.6, 128.8, 126.9, 120.5, 68.6, 23.9; HRMS (ESI): [M + H]$^+$ calcd for C$_{11}$H$_{11}$O$_2$: m/z 175.0754, found: 175.0751.

References

Copies of $^1$H NMR, $^{13}$C NMR and NOESY spectra

(1d)
(1j)
(1k)
$2,4-(\text{Me})_2\text{C}_6\text{H}_3^+\text{O}^\\text{Me}\text{CO}_2\text{Et}$

(3h)
NOESY (δ 6.10 and 2.22)
(2d)
(21)
(2m)
(2n)
4-MeC₆H₄

(2o)
(4c)
NOESY (δ 5.89 and 2.27)
NOESY (δ 5.86 and 2.23)
NOESY (δ 5.90 and 2.28)
NOESY ($\delta$ 5.88 and 2.26)
NOESY (δ 5.86 and 2.23)
NOESY (δ 5.88 and 2.26)