Visible light-Induced Intermolecular Addition Reactions between Alkyl-Bromocarboxylates and Enamines

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1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. Anhydrous DMF, CH₃CN, DMSO, DCM were freshly distilled from calcium hydride, Anhydrous PhMe was freshly distilled from Sodium. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz spectrometer. The chemical shifts for ¹H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ¹³C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.00 ppm) as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. Analytical GC was performed on an Agilent 7890A with FID detector. HRMS were performed under ESI ionization technique on a Waters Micromass Q-TOF Premier Mass Spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh).

2. Preparation of substrates

2.1 Representative procedure for the preparation of enamines. (1a-1l)

To a solution of acetophenone (10.0 g, 86.0 mmol) and piperidine (42.5 g, 516.0 mmol) in anhydrous hexane (200 mL), was added TiCl₄ (17.8 g, 86.0 mmol) over 30 min at 0 °C. The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was evaporated under vacuum to give colorless oil, which was distilled under reduced pressure (1 mmHg, 99 °C) to give N-(1-styryl)piperidine (1b) as a pale yellow liquid (12.0 g, 82% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.45 (m, 2H), 7.33–7.28 (m, 3H), 4.24 (s, 1H), 4.15 (s, 1H), 2.82–2.79 (m, 4H), 1.62–1.53 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.0, 140.3, 128.0, 127.7, 127.7, 90.1, 50.5, 26.0, 24.5.

2.2 A General procedure for the preparation of cinnamyl 2-bromopropanoate.

To a mixture of 5.9 g (80.0 mmol) of propionic acid and 4.3 g (16.0 mmol) of tribromophosphine in a 50 ml three-necked flask, bromine (25.6 g, 160.1 mmol) was added dropwise at 80 °C over 30 min. After the addition is complete, the solution was heated over a
period of 3 hours. The excess bromine and hydrogen bromide are removed under reduced pressure. To a solution of 4.0 g (30.0 mmol) of cinnamyl alcohol, 0.4 g (3.0 mmol) of DMAP and 4.8 g (60.0 mmol) of pyridine in 30 mL DCM was cooled at 0 °C. The α-bromopropanoyl bromide was added dropwise slowly at such a rate to maintain the internal temperature blow 20 °C for 30 min. After completion, the reaction was quenched with H2O (30 mL) and extracted with DCM (3×30 mL). The combined organic extracts were dried over Na2SO4 and the solvent was removed under reduced pressure. The crude product was purified by silica-gel column chromatography to give cinnamyl 2-bromopropanoate as pale yellow oil (5.7 g, 70% yield). 1H NMR (400 MHz, CDCl3) δ 7.44–7.24 (m, 5H), 6.71 (d, J = 16.0 Hz, 1H), 6.29 (dt, J = 15.6, 6.4 Hz, 1H), 4.83 (dd, J = 6.0, 0.8 Hz, 2H), 4.42 (q, J = 6.8 Hz, 1H), 1.86 (d, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 169.9, 135.9, 134.8, 128.5, 128.1, 126.6, 122.1, 66.3, 40.0, 21.6.

2.3 A General procedure for the preparation of allyl 2-bromo-2-phenylacetate.7

To a mixture of 17.7 g (130.0 mmol) of phenylacetic acid and 7.0 g (26.0 mmol) of tribromophosphine in a 100 mL three-necked flask, the bromine (41.6 g, 260.0 mmol) was added dropwise at 100 °C over 30 min. After the addition is complete, the solution was heated over a period of 4 hours. The excess bromine and hydrogen bromide are removed under reduced pressure. To a solution of 7.6 g (130.0 mmol) of allyl alcohol and 13.8 g (136.5 mmol) of Et3N in 30 mL DCM was cooled at 0 °C. The solution of 2-bromo-2-phenylacetyl bromide in 20 mL was added dropwise slowly at such a rate to maintain the internal temperature blow 20 °C for 30 min. After 1h, the reaction was quenched with H2O (50 mL) and extracted with DCM (3×50 mL). The combined organic extracts were dried over Na2SO4 and the solvent was removed under reduced pressure to give colorless oil, which was distilled under reduced pressure (2 mmHg, 100 °C) to give allyl 2-bromo-2-phenylacetate as a colorless oil (17.5 g, 53% yield). 1H NMR (400 MHz, CDCl3) δ 7.57–7.53 (m, 2H), 7.38–7.34 (m, 3H), 5.95–5.85 (m, 1H), 5.38 (s, 1H), 5.32 (dq, J = 17.2, 1.6 Hz, 1H), 5.25 (dq, J = 10.4, 1.2 Hz, 1H), 4.69–4.66 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 167.8, 135.6, 131.0, 129.2, 128.7, 128.6, 118.9, 66.7, 46.5.
3. A general procedure for Ru(bpy)$_3$Cl$_2$-catalyzed reaction between enamines and alkyl bromocarboxylates under visible light

A dried Schlenk tube equipped with a stirrer bar which was evacuated and backfilled with nitrogen was added alkyl bromocarboxylate (1.0 mmol, 181.0 mg), K$_2$CO$_3$ (0.5 mmol, 69 mg), Ru(bpy)$_3$Cl$_2$ (0.01 mmol, 7.48 mg), Et$_3$N (0.2 mmol, 20.4 mg), 4-methoxypyridine (0.2 mmol, 218.2 mg) and enamine (0.5 mmol). Then 2 mL of DMF was added into the reaction tube via a syringe. The reaction mixture was degassed by the freeze-pump-thaw method and then irradiated with a 23W fluorescent household light bulb (distance app. 5 cm) for 24 h. After the completion of the reaction, it was quenched by water and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined and the pure product was obtained by flash column chromatography on silica gel.

4. The control experiment of the reaction conducted in the different temperature in the dark.$^a$

$$
\begin{array}{c|c}
\text{reaction temp. (°C)} & \text{yield$^b$ (%)} \\
40 & 5 \\
60 & 10 \\
80 & 8 \\
100 & 5 \\
\end{array}
$$

$^a$Conditions: 1b (0.5 mmol), 2a (1 mmol), Et$_3$N (0.2 mmol), 4-methoxypyridine (0.2 mmol), base (0.5 mmol), solvent (2 mL), heated from 40 to 100 °C for 24 h. $^b$Isolated yields.
5. Spectral data for substrates and products

5.1. Spectral data for substrates

N-(1-phenylvinyl)morpholine

Pale yellow liquid, 86% yield (1 mmHg, 120 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48–7.45 (m, 2H), 7.33–7.31 (m, 3H), 4.33 (s, 1H), 4.19 (s, 1H), 3.78–3.76 (m, 4H), 2.84–2.82 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.0, 139.0, 128.1, 128.0, 127.7, 91.0, 66.8, 49.7.

N-(1-phenylvinyl)piperidine

Pale yellow liquid, 82% yield (1 mmHg, 99 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48–7.45 (m, 2H), 7.33–7.28 (m, 3H), 4.24 (s, 1H), 4.15 (s, 1H), 2.82–2.79 (m, 4H), 1.62–1.53 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.0, 140.3, 128.0, 127.7, 127.7, 90.1, 50.5, 26.0, 24.5.

N-(1-phenylvinyl)pyrrolidine

Pale yellow liquid, 86% yield (1 mmHg, 120 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48–7.45 (m, 2H), 7.33–7.31 (m, 3H), 4.33 (s, 1H), 4.19 (s, 1H), 3.78–3.76 (m, 4H), 2.84–2.82 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.0, 139.0, 128.1, 128.0, 127.7, 91.0, 66.8, 49.7.
Pale yellow liquid, 88% yield (1 mmHg, 96 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43–7.41 (m, 2H), 7.36–7.31 (m, 3H), 3.89 (s, 1H), 3.85 (s, 1H), 3.04–3.00 (m, 4H), 1.91–1.88 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.3, 140.5, 127.7, 127.7, 127.4, 84.2, 49.1, 24.9.

N,N-diethyl-1-phenylethenamine

Pale yellow liquid, 85% yield (1 mmHg, 60–61 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45–7.41 (m, 2H), 7.33–7.28 (m, 3H), 4.15 (s, 1H), 4.06 (s, 1H), 2.99 (q, $J = 7.2$ Hz, 4H), 1.03 (t, $J = 7.2$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.0, 141.0, 128.5, 128.2, 127.9, 127.9, 127.6, 90.1, 43.1, 11.6.

N-(1-(p-tolyl)vinyl)piperidine

Pale yellow liquid, 79% yield (0.1 mmHg, 78 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37–7.34 (m, 2H), 7.14–7.12 (m, 2H), 4.21 (s, 1H), 4.10 (s, 1H), 2.81–2.78 (m, 4H), 2.35 (s, 3H), 1.64–1.58 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.0, 137.5, 137.4, 128.7, 127.6, 89.5, 50.5, 6.0, 24.5, 21.1.

N-(1-(4-fluorophenyl)vinyl)piperidine

Pale yellow liquid, 83% yield (1 mmHg, 125 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46–7.40 (m, 2H), 7.03–6.97 (m, 2H), 4.20 (s, 1H), 4.13 (s, 1H), 2.76–2.79 (m, 4H), 1.64–1.52 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.7, 161.3, 157.0, 136.2, 129.2, 129.1, 114.9, 114.7, 90.3,
50.5, 26.0, 24.4. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -115.23. HRMS-ESI (m/z): Calculated for C$_{13}$H$_{16}$FN (M + H)$^+$: 206.1345, Found: 206.1330.

**N-(1-(4-chlorophenyl)vinyl)piperidine$^5$**

![Chemical Structure](image1.png)

Pale yellow liquid, 75% yield (0.06 mmHg, 80–83 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44–7.40 (m, 2H), 7.32–7.28 (m, 2H), 4.25 (s, 1H), 4.17 (s, 1H), 2.81–2.78 (m, 4H), 1.66–1.57 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.9, 138.8, 133.4, 128.9, 128.2, 90.8, 50.5, 25.9, 24.4.

**N-(1-(4-(trifluoromethyl)phenyl)vinyl)piperidine**

Pale yellow liquid, 79% yield (1 mmHg, 128 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (s, 4H), 4.30 (s, 1H), 4.23 (s, 1H), 2.79–2.77 (m, $J = 5.6$ Hz, 4H), 1.65–1.52 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.8, 144.0, 130.1, 130.0, 129.7, 129.6, 129.4, 129.3, 127.9, 125.59, 125.0, 122.8, 91.9, 50.5, 25.9, 24.4. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.86. HRMS-ESI (m/z): Calculated for C$_{14}$H$_{16}$F$_3$N (M + H)$^+$: 256.1313, Found: 256.1301.

**N-(1-(4-methoxyphenyl)vinyl)piperidine$^5$**

Pale yellow liquid, 72% yield (0.1 mmHg, 92–94 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40–7.26 (m, 2H), 6.87–6.83 (m, 2H), 4.18 (s, 1H), 4.08 (s, 1H), 3.81 (s, 3H), 2.81–2.78 (m, 4H), 1.63–1.54 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.4, 157.6, 132.7, 128.7, 113.36, 89.0, 77.3, 77.0, 76.7, 55.2, 50.5, 26.0, 24.6.

**N-(1-(o-tolyl)vinyl)piperidine**
Pale yellow liquid, 83% yield (1 mmHg, 125 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23–7.11 (m, 4H), 4.13 (s, 1H), 3.83 (s, 1H), 2.79–2.77 (m, 4H), 2.35 (s, 3H), 1.56–1.52 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.4, 140.2, 136.4, 129.8, 129.6, 127.3, 125.2, 87.6, 48.8, 25.8, 24.5, 19.8. HRMS-ESI (m/z): Calculated for C$_{14}$H$_{19}$N (M + H)$^+$: 202.1596, Found: 202.1656.

N-(1-phenylprop-1-en-1-yl)piperidine$^6$

Pale yellow liquid, 80% yield (1 mmHg, 95–97 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34–7.33 (m, 3H), 7.29–7.26 (m, 2H), 4.67 (q, $J$ = 6.8 Hz, 1H), 2.68–2.66 (m, 4H), 1.59–1.49 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.1, 138.6, 129.7, 127.8, 127.1, 99.1, 50.6, 26.2, 24.6, 13.9. HRMS-ESI (m/z): Calculated for C$_{14}$H$_{19}$N (M + H)$^+$: 202.1596, Found: 202.1664.

N-(3,4-dihydronaphthalen-1-yl)piperidine$^6$

Pale yellow liquid, 70% yield (0.7 mmHg, 120–125 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, $J$ = 7.2 Hz, 1H), 7.22–7.17 (m, 1H), 7.14–7.12 (m, 2H), 5.24 (t, $J$ = 4.8 Hz, 1H), 2.76 (s, 4H), 2.69–2.65 (m, 2H), 2.26–2.18 (m, 2H), 1.71 (dd, $J$ = 11.6, 6.0 Hz, 4H), 1.57 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.6, 138.0, 132.9, 127.5, 126.5, 126.0, 123.4, 106.7, 52.0, 28.7, 26.3, 24.7, 22.5. HRMS-ESI (m/z): Calculated for C$_{15}$H$_{19}$N (M + H)$^+$: 214.1596, Found: 214.1628.

cinnamyl 2-bromopropanoate$^7$
Pale yellow oil, 70% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44–7.24 (m, 5H), 6.71 (d, $J$ = 16.0 Hz, 1H), 6.29 (dt, $J$ = 15.6, 6.4 Hz, 1H), 4.83 (dd, $J$ = 6.0, 0.8 Hz, 2H), 4.42 (q, $J$ = 6.8 Hz, 1H), 1.86 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9, 135.9, 134.8, 128.5, 128.1, 126.6, 122.1, 66.3, 40.0, 21.6.

**allyl 2-bromo-2-phenylacetate**

Colorless oil, 53% yield (2 mmHg, 100 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57–7.53 (m, 2H), 7.38–7.34 (m, 3H), 5.95–5.85 (m, 1H), 5.38 (s, 1H), 5.32 (dq, $J$ = 17.2, 1.6 Hz, 1H), 5.25 (dq, $J$ = 10.4, 1.2 Hz, 1H), 4.69–4.66 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.8, 135.6, 131.0, 129.2, 128.7, 128.6, 118.9, 66.7, 46.5.

5.2. Spectral data for products

**ethyl 2-methyl-4-oxo-4-phenylbutanoate**

Yellow liquid, 94% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00–7.92 (m, 2H), 7.59–7.53 (m, 1H), 7.51–7.41 (m, 2H), 4.15 (q, $J$ = 7.2 Hz, 2H), 3.48 (dd, $J$ = 17.6, 8.0 Hz, 1H), 3.16–3.06 (m, 1H), 3.00 (dd, $J$ = 17.6, 5.6 Hz, 1H), 1.29–1.22 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.0, 175.9, 136.7, 133.1, 128.5, 127.9, 60.5, 41.9, 35.0, 17.2, 14.1.

**ethyl 2-methyl-4-oxo-4-(p-tolyl)butanoate**

Yellow liquid, 92% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94–7.79 (m, 2H), 7.26–7.24 (m,
2H), 4.14 (q, J = 7.2 Hz, 2H), 3.44 (dd, J = 17.6, 8.0 Hz, 1H), 3.15–3.05 (m, 1H), 2.98 (dd, J = 17.6, 5.6 Hz, 1H), 2.40 (s, 3H), 1.28–1.22 (m, 6H). 13C NMR (100 MHz, CDCl3) δ 197.4, 175.7, 143.7, 134.1, 129.0, 127.9, 60.3, 41.6, 34.9, 21.4, 17.1, 14.0. HRMS-ESI (m/z): Calculated for C14H18O3 (M + H)+: 235.1334, Found: 235.1337.

**ethyl 4-(4-fluorophenyl)-2-methyl-4-oxobutanoate**

![Structure 3f](image)

Yellow liquid, 92% yield. 1H NMR (400 MHz, CDCl3) δ 8.04–7.95 (m, 2H), 7.17–7.09 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.45 (dd, J = 17.6, 8.0 Hz, 1H), 3.16–3.06 (m, 1H), 2.96 (dd, J = 17.6, 5.6 Hz, 1H), 1.26 (dd, J = 14.4, 7.2 Hz, 6H). 13C NMR (100 MHz, CDCl3) δ 196.4, 175.8, 166.9, 164.4, 133.1, 130.6, 130.5, 115.7, 115.5, 60.5, 41.7, 35.0, 17.2, 14.1. 19F NMR (376 MHz, CDCl3) δ -105.57. HRMS-ESI (m/z): Calculated for C13H15FO3 (M + Na)+: 261.0903, Found: 261.0707.

**ethyl 4-(4-chlorophenyl)-2-methyl-4-oxobutanoate**

![Structure 3g](image)

Yellow liquid, 91% yield. 1H NMR (400 MHz, CDCl3) δ 7.96–7.88 (m, 2H), 7.47–7.40 (m, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.45 (dd, J = 17.6, 8.0 Hz, 1H), 3.15–3.06 (m, 1H), 2.95 (dd, J = 17.6, 5.2 Hz, 1H), 1.30–1.22 (m, 6H). 13C NMR (100 MHz, CDCl3) δ 196.8, 175.7, 139.5, 134.9, 129.3, 128.8, 60.5, 41.7, 34.9, 17.2, 14.0.

**ethyl 2-methyl-4-oxo-4-(4-(trifluoromethyl)phenyl)butanoate**

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Yellow liquid, 78% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 8.2$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 4.15 (q, $J = 7.2$ Hz, 2H), 3.51 (dd, $J = 17.6$, 8.0 Hz, 1H), 3.18–3.09 (m, 1H), 2.99 (dd, $J = 17.6$, 5.2 Hz, 1H), 1.31–1.23 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.2, 175.6, 139.3, 134.5, 134.2, 128.3, 125.6, 125.5, 124.9, 122.2, 60.6, 42.1, 35.0, 17.2, 14.2. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.55. HRMS-ESI (m/z): Calculated for C$_{14}$H$_{15}$F$_3$O$_3$ (M + H)$^+$: 289.1052, Found: 289.1064.

**ethyl 4-(4-methoxyphenyl)-2-methyl-4-oxobutanoate**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97–7.93 (m, 2H), 6.95–6.91 (m, 2H), 4.15 (q, $J = 6.8$ Hz, 2H), 3.87 (s, 3H), 3.43 (dd, $J = 17.2$, 8.0 Hz, 1H), 3.15–3.06 (m, 1H), 2.97 (dd, $J = 17.2$, 5.6 Hz, 1H), 1.29–1.22 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 176.0, 163.4, 130.2, 129.7, 113.6, 60.4, 55.3, 41.4, 35.0, 17.2, 14.0.

**ethyl 2-methyl-4-oxo-4-(o-tolyl)butanoate**

Yellow liquid, 97% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.36 (td, $J = 7.2$, 1.2 Hz, 1H), 7.28–7.21 (m, 2H), 4.15 (q, $J = 7.2$ Hz, 2H), 3.40 (dd, $J = 17.6$, 8.0 Hz, 1H), 3.14–3.05 (m, 1H), 2.91 (dd, $J = 17.6$, 5.6 Hz, 1H), 2.48 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.0, 175.8, 138.0, 137.6, 131.8, 131.2, 128.4, 125.6, 60.5, 44.7, 35.2, 21.2, 17.2, 14.1. HRMS-ESI (m/z): Calculated for C$_{14}$H$_{18}$O$_3$ (M + Na)$^+$: 257.1154, Found: 257.1155.
ethyl 2,3-dimethyl-4-oxo-4-phenylbutanoate

\[\text{3k}\]

Yellow liquid, 66% yield, dr = 11:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02–7.92 (m, 2H), 7.60–7.53 (m, 1H), 7.51–7.42 (m, 2H), 4.15–3.96 (m, 2H), 3.80–3.72 (m, 1H), 3.02–2.89 (m, 1H), 1.29–1.12 (m, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 203.4, 175.7, 136.0, 132.9, 128.6, 128.3, 60.5, 43.0, 41.7, 14.5, 14.1, 14.0.

ethyl 2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propanoate

\[\text{3l}\]

Yellow liquid, 33% yield, dr = 3:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) for major \(\delta\) 8.02 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.47 (td, \(J = 11.2, 1.2\) Hz, 1H), 7.30 (t, \(J = 7.6\) Hz, 1H), 7.24 (d, \(J = 7.6\) Hz, 1H), 4.23–4.16 (m, 2H), 3.22–2.98 (m, 4H), 2.21–2.15 (m, 1H), 1.99–1.88 (m, 1H), 1.29 (t, \(J = 7.2\) Hz, 3H), 1.17 (d, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 198.0, 176.0, 143.9, 133.3, 132.3, 128.6, 127.4, 126.6, 60.5, 50.2, 38.7, 29.4, 25.2, 14.2, 13.1.

methyl 2-methyl-4-oxo-4-phenylbutanoate

\[\text{3m}\]

Yellow liquid, 90% yield, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98–7.95 (m, 2H), 7.59–7.53 (m, 1H), 7.51–7.41 (m, 2H), 3.70 (s, 3H), 3.51–3.44 (m, 1H), 3.14 (qd, \(J = 7.2, 1.6\) Hz, 1H), 3.02 (dd, \(J = 17.6, 5.6\) Hz, 1H), 1.29–1.27 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.9, 176.3, 136.5, 133.0, 128.5, 127.9, 51.8, 41.9, 34.8, 17.2.

isopropyl 2,2-dimethyl-4-oxo-4-phenylbutanoate
Yellow liquid, 78% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03–8.00 (m, 2H), 7.60–7.55 (m, 1H), 7.51–7.45 (m, 2H), 4.36–4.28 (m, 1H), 4.13–4.04 (m, 4H), 2.83 (dd, $J = 16.4$, 7.2 Hz, 2H), 2.51 (dd, $J = 16.4$, 6.8 Hz, 2H), 1.19 (t, $J = 7.2$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.0, 171.4, 135.8, 133.2, 128.7, 128.5, 60.8, 38.7, 36.0, 29.7, 14.0. HRMS-ESI (m/z): Calculated for C$_{15}$H$_{20}$O$_3$ (M + H)$^+$: 249.1491, Found: 249.1482.

**ethyl 2,2-dimethyl-4-oxo-4-phenylbutanoate**

Yellow liquid, 62% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95–7.92 (m, 2H), 7.57–7.53 (m, 1H), 7.47–7.43 (m, 2H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.28 (s, 2H), 1.32 (s, 6H), 1.20 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.6, 177.2, 137.0, 132.9, 128.5, 127.8, 60.4, 48.4, 40.0, 29.6, 25.7, 14.0.

**ethyl 4-oxo-4-phenylbutanoate**

Yellow liquid, 66% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01–7.92 (m, 2H), 7.59–7.52 (m, 1H), 7.50–7.42 (m, 2H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.31 (t, $J = 6.4$ Hz, 2H), 2.75 (t, $J = 6.4$ Hz, 2H), 1.26 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.0, 172.7, 136.5, 128.5, 127.9, 60.5, 33.3, 28.2, 14.0.

**cinnamyl 2-methyl-4-oxo-4-phenylbutanoate**
Yellow liquid, 68% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98–7.96 (m, 2H), 7.58–7.24 (m, 9H), 6.65 (d, $J = 16.0$ Hz, 1H), 6.27 (dt, $J = 15.6, 6.4$ Hz, 1H), 4.76 (dt, $J = 6.4$ Hz, 1.6, 2H), 3.51 (dd, $J = 17.6, 8.0$ Hz, 1H), 3.22–3.16 (m, 1H), 3.05 (dd, $J = 17.6, 5.6$ Hz, 1H), 1.32 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.9, 175.6, 136.5, 136.2, 133.8, 133.1, 128.5, 128.5, 127.9, 127.9, 126.5, 123.1, 65.1, 41.8, 35.0, 17.3. HRMS-ESI (m/z): Calculated for C$_{20}$H$_{20}$O$_3$ (M + H)$^+$: 309.1491, Found: 309.1481.

allyl 4-oxo-2,4-diphenylbutanoate$^{14}$

Yellow liquid, 77% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (m, 2H), 7.60–7.26 (m, 8H), 5.92–5.78 (m, 1H), 5.24–5.14 (m, 2H), 4.67–4.55 (m, 2H), 4.33 (dd, $J = 10.4, 4.4$ Hz, 1H), 3.96 (dd, $J = 18.0, 10.4$ Hz, 1H), 3.29 (dd, $J = 18.0, 4.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.5, 173.0, 138.2, 136.3, 133.3, 131.9, 128.8, 128.5, 128.0, 127.8, 127.5, 117.8, 65.5, 46.4, 42.7.

6. Reference

1 W. J. Zhao, M. Yan, D. Huang and S. J. Ji, Tetrahedron, 2005, 61, 5585.
7. The NOE experiment of N-(1-phenylprop-1-en-1-yl)piperidine (1I)
8. NMR spectra of the products

N-(1-phenylvinyl)morpholine (1a)

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

N-(1-phenylvinyl)piperidine (1b)

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \]
N-(1-phenylvinyl)pyrrolidine (1c)

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

$^1$C NMR (100 MHz, CDCl$_3$)
N,N-diethyl-1-phenylethenamine (1d)

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

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{)} \]
N-(1-(p-tolylvinyl)piperidine (1e)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(1-(4-fluorophenyl)vinyl)piperidine (1f)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (376 MHz, CDC$_3$)
N-(1-(4-chlorophenyl)vinyl)piperidine (1g)

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

\[ \text{\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \] } \]
N-(1-(4-(trifluoromethyl)phenyl)vinyl)piperidine (1h)
$^{19}$F NMR (376 MHz, CDCl$_3$)
N-(1-(4-methoxyphenyl)vinyl)piperidine (1i)

\[ \text{MeO} \quad 1i \]

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

\[ \text{MeO} \quad 1i \]

$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(1-(o-tolyl)vinyl)piperidine (1j)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(1-phenylprop-1-en-1-yl)piperidine (1k)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(3,4-dihydronaphthalen-1-yl)piperidine (1l)

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

$^13$C NMR (100 MHz, CDCl$_3$)
allyl 2-bromo-2-phenylacetate (2r)

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

$\text{C NMR (100 MHz, CDCl}_3\text{)}$
cinnamyl 2-bromopropanoate (2q)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
ethyl 2-methyl-4-oxo-4-phenylbutanoate (3b)

\[
\text{\textbf{3b}} \\
\text{\textsuperscript{1}H NMR (400 MHz, CDCl₃)}
\]

\[
\text{\textbf{3b}} \\
\text{\textsuperscript{13}C NMR (100 MHz, CDCl₃)}
\]
ethyl 2-methyl-4-oxo-4-(p-tolyl)butanoate (3e)

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

$^{13}C$ NMR (100 MHz, CDCl$_3$)
ethyl 4-(4-fluorophenyl)-2-methyl-4-oxobutanoate (3f)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
ethyl 4-(4-chlorophenyl)-2-methyl-4-oxobutanoate (3g)
ethyl 2-methyl-4-oxo-4-(4-(trifluoromethyl)phenyl)butanoate (3h)
$^{19}$F NMR (376 MHz, CDCl$_3$)
ethyl 4-(4-methoxyphenyl)-2-methyl-4-oxobutanoate (3i)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
ethyl 2-methyl-4-oxo-4-(o-tolyl)butanoate (3j)

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

$^13$C NMR (100 MHz, CDCl$_3$)
ethyl 2,3-dimethyl-4-oxo-4-phenylbutanoate (3k)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
ethyl 2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propanoate (3l)

\[ \text{3l} \]

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

\[ \text{3l} \]

$^{13}$C NMR (100 MHz, CDCl$_3$)
methyl 2-methyl-4-oxo-4-phenylbutanoate (3m)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
isopropyl 2,2-dimethyl-4-oxo-4-phenylbutanoate (3n)

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

$^{13}$C NMR (100 MHz, CDCl$_3$)
ethyl 2,2-dimethyl-4-oxo-4-phenylbutanoate (3o)

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

\[ \text{C NMR (100 MHz, CDCl}_3) \]
ethyl 4-oxo-4-phenylbutanoate (3p)

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

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \]

- 35.00
- 136.00
- 172.30
- 77.70
- 76.60
- 46.65
- 33.95
- 28.65
- 14.65

\[ \text{3p} \]
cinnamyl 2-methyl-4-oxo-4-phenylbutanoate (3q)

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

$\text{C NMR (100 MHz, CDCl}_3\}$
allyl 4-oxo-2,4-diphenylbutanoate (3r)

1H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)