Supporting Information

Hydrogen Peroxide and Anhydride Prompted Transformation of Enamides into α-Acyloxy Ketones via Acyl Intramolecular Migration Process

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General Remarks

$^{1}$H-NMR spectra were recorded on Bruker avance III-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). Products were purified by flash chromatography on 200–300 mesh silica gels. All melting points were determined without correction. Commercially available reagents and solvents were used without further purification. Unless otherwise noted, the enamides 1 were in all cases prepared from the corresponding ketoximes according to reported literature$^1$. Ethyl 2-acetamidoacrylate 1x was prepared according to the reported literature$^2$. N-(1-phenylvinyl)benzamide 1ae was prepared according to the reported literature$^3$.

Preparation of deuterated enamide substrates $d$-1a and $d$5-1a$^3$

A solution of N-(1-Phenylvinyl)acetamide (1a, 322 mg, 2 mmol) in CD$_3$OD (0.6 mL) was stirred at room temperature for 12 h and then concentrated under reduced pressure to afford the deuterated product $d$-1a as white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.36 (m, 5 H), 6.98 (m, 0.3 H), 5.86 (m, 1 H), 5.08 (s, 1 H), 2.11 (s, 3 H).

NaH (120 mg, 3 mmol, 1.5 equiv, 60 wt %) was added to the solution of N-(1-Phenylvinyl)acetamide (1a, 322 mg, 2 mmol, 1.0 equiv) in DMF (2 mL) at 0 °C. The
reaction mixture was warmed to room temperature and stirred overnight. CD$_3$OD (0.6 mL) was added dropwise and the resulting mixture was stirred for 2 h at room temperature. Then quenched by addition of water (5 mL) and EtOAc (8 mL). The organic layer was separated, washed with water, dried over sodium sulfate, concentrated and purified by column chromatography to afford $d_5$-1a as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.36 (m, 5 H), 6.98 (m, 1 H), 5.89 (s, 0.7 H), 5.09-5.07 (m, 0.7 H), 2.11 (s, 2 H).

**Preparation of N-ethyl enamide substrates 1ag**

1 mmol (1 equiv) of enamide was dissolved in 5 mL of anhydrous DMF in a screw cap via under argon atmosphere. The solution was cooled to 0 °C and 1.5 mmol (1.5 equiv) of sodium hydride (60% dispersion in mineral oil) was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Iodoethane (2 mmol, 2 equiv) was then added dropwise. The final solution was warmed to room temperature and continued to stir for overnight. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding water at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layers were concentrated under reduced pressure and the pure product was isolated by flash column chromatography (hexane/ethyl acetate) to afford the corresponding product 1ag.


**General experimental procedure**

A test tube equipped with a magnetic stir bar was charged with enamide 1a (32.2 mg, 0.2 mmol), H$_2$O$_2$ (30% in water) (113.3 mg, 1.0 mmol) and Ac$_2$O (102.0 mg 1.0 mmol). Then the reaction mixture was stirred at room temperature under air with a water bath. After completion of the reaction (monitored by TLC), the mixture was extracted with ethyl acetate and washed with NaOH (0.4 mol/L, 6 mL) and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo, the residues were purified by column chromatography, eluting with petroleum ether/EtOAc to give the desired product 2a as colorless oil.

**Experimental procedure for Table 1, entry 14**

A schlenk tube equipped with a magnetic stir bar was charged with enamide 1a (32.2 mg, 0.2 mmol), and Ac$_2$O (102.0 mg, 1.0 mmol). The reaction tube was evacuated and backfilled with N$_2$ (3 times, balloon), Then H$_2$O$_2$ (30% in water) (113.3 mg, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature with a water bath for 10 min, the mixture was extracted with ethyl acetate and washed with NaOH (0.4 mol/L, 6 mL) and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo the residues were purified by column chromatography, eluting with petroleum ether/EtOAc to give the pure product 2a.
Experimental procedure for Table 1, entry 15

H$_2$O$_2$ (30% in water, 20 mmol) was added to a solution of enamide 1a (10 mmol) in Ac$_2$O (20 mmol) at 0 °C under air. The reaction mixture was warmed to room temperature and stirred for 1 h. After completion of the reaction (monitored by TLC), the mixture was extracted with ethyl acetate and washed with NaOH and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo and purified by column chromatography to afford desired product 2a as white solid with 83% yield.

Analytical Data for Products.

2-oxo-2-phenylethyl acetate (2a)$^5$

Colorless oil (90%, 32.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.90 (m, 2 H), 7.63-7.59 (t, $J$ = 7.6 Hz, 1 H), 7.50-7.46 (t, $J$ = 7.6 Hz, 2 H), 5.34 (s, 2 H), 2.23 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.13, 170.41, 134.18, 133.87, 128.84, 127.73, 65.99, 20.55. EI-MS: m/z 178.

2-oxo-2-(p-tolyl)ethyl acetate (2b)$^5$

White solid (73%, 28.0 mg), melting point: 80–82 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82-7.80 (d, $J$ = 8.0 Hz, 2 H), 7.29-7.27 (d, $J$ = 8.0 Hz, 2 H), 5.32 (s, 2 H), 2.42 (s, 3 H), 2.23 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.72, 170.43, 144.82, 131.67, 129.48,
2-oxo-2-(m-tolyl)ethyl acetate (2c)

Colorless oil (86%, 33.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72-7.69 (m, 2 H), 7.42-7.34 (m, 2 H), 5.33 (s, 2 H), 2.41 (s, 3 H), 2.23 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.27, 170.40, 138.71, 134.61, 134.18, 128.66, 128.21, 124.86, 66.01, 21.26, 20.53. EI-MS: m/z 192.

2-oxo-2-(o-tolyl)ethyl acetate (2d)

Colorless oil (73%, 27.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62-7.59 (m, 1 H), 7.44-7.40 (m, 1 H), 7.29-7.26 (m, 2 H), 5.18 (s, 2 H), 2.51 (s, 3 H), 2.21 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.75, 170.41, 139.04, 134.32, 132.22, 132.12, 128.00, 125.72, 67.26, 21.07, 20.50. EI-MS: m/z 192.

2-(4-methoxyphenyl)-2-oxoethyl acetate (2e)

Yellow oil (36%, 15.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.88 (m, 2 H), 6.98-6.94 (m 2 H), 5.30 (s, 2 H), 3.88 (s, 3 H), 2.23 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.58, 170.50, 164.02, 130.04, 127.18, 114.02, 65.73, 55.51, 20.60. EI-MS: m/z 208.
2-(3-methoxyphenyl)-2-oxoethyl acetate (2f)<sup>8</sup>

![Structure](image)

Colorless oil (60%, 25.0 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48-7.44 (m, 2 H), 7.41-7.37 (m, 1 H), 7.16-7.13 (m, 1 H), 5.32 (s, 2 H), 3.85 (s, 3 H), 2.23 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.96, 170.38, 159.93, 135.41, 129.82, 120.36, 120.11, 112.01, 66.05, 55.43, 20.53. EI-MS: m/z 208.

2-(2-methoxyphenyl)-2-oxoethyl acetate (2g)<sup>9</sup>

Yellow solid (53%, 22.0 mg), melting point: 58–60 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.92 (m, 1 H), 7.55-7.50 (m, 1 H), 7.06-6.98 (m, 2 H), 5.24 (s, 2 H), 3.94 (s, 3 H), 2.21 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.00, 170.57, 159.46, 134.88, 131.01, 124.30, 121.00, 111.45, 69.96, 55.52, 20.62. EI-MS: m/z 208.

2-(4-(tert-butyl)phenyl)-2-oxoethyl acetate (2h)<sup>6</sup>

Colorless oil (77%, 36.0 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.85 (m, 2 H), 7.52-7.49 (m, 2 H), 5.34 (s, 2 H), 2.24 (s, 3 H), 1.34 (s, 9 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.69, 170.43, 157.71, 131.48, 127.65, 125.76, 65.93, 35.16, 30.95, 20.57. EI-MS: m/z 234.
2-([1,1′-biphenyl]-4-yl)-2-oxoethyl acetate (2i): White solid (71%, 36.0 mg), melting point: 96–98 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00-7.97 (m, 2 H), 7.71-7.69 (m, 2 H), 7.63-7.61 (m, 2 H), 7.49-7.45 (m, 2 H), 7.42-7.38 (m, 1 H), 5.36 (s, 2 H), 2.24 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 191.73, 170.44, 146.56, 139.57, 132.83, 128.97, 128.40, 128.32, 127.43, 127.24, 66.00, 20.56. EI-MS: m/z 254.

2-(naphthalen-1-yl)-2-oxoethyl acetate (2j): Yellow solid (61%, 27.8 mg), melting point: 88–90 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.64-8.62 (d, \(J = 8.4\) Hz, 1 H), 8.04-8.02 (d, \(J = 8.0\) Hz, 1 H), 7.89-7.84 (m, 2 H), 7.63-7.48 (m, 3 H), 5.31 (s, 2 H), 2.25 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 196.07, 170.51, 133.90, 133.51, 132.30, 130.17, 128.44, 128.33, 127.43, 126.75, 125.50, 124.19, 67.46, 20.57. EI-MS: m/z 228.

2-(naphthalen-2-yl)-2-oxoethyl acetate (2k): White solid (67%, 30.6 mg), melting point: 68–70 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.41 (s, 1 H), 7.97-7.86 (m, 4 H), 7.64-7.54 (m, 2 H), 5.47 (s, 2 H), 2.25 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 192.05, 170.46, 135.83, 132.31, 131.46, 129.51, 129.44, 128.83, 128.78, 127.83, 127.01, 123.21, 66.05, 20.58. EI-MS: m/z 228.
2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-oxoethyl acetate (2l)

Colorless oil (72%, 34.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.43 (m, 2 H), 6.93-6.91 (m, 1 H), 5.27 (s, 2 H), 4.33-4.31 (m, 2 H), 4.29-4.27 (m, 2 H), 2.22 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.44, 170.39, 148.59, 143.48, 127.77, 121.75, 117.44, 117.17, 65.71, 64.62, 63.99, 20.54. EI-MS: m/z 236.

2-(4-chlorophenyl)-2-oxoethyl acetate (2m)$^5$

White solid (87%, 36.9 mg), melting point: 70–72 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87-7.83 (m, 2 H), 7.48-7.44 (m, 2 H), 5.30 (s, 2 H), 2.22 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.06, 170.33, 140.33, 132.43, 129.17, 129.11, 65.79, 20.46. EI-MS: m/z 212.

2-(3-chlorophenyl)-2-oxoethyl acetate (2n)$^6$

Colorless oil (71%, 30.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90-7.88 (m, 1 H), 7.80-7.78 (m, 1 H), 7.60-7.57 (m, 1 H), 7.46-7.42 (m, 1 H), 5.31 (s, 2 H), 2.24 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.04, 170.35, 135.54, 135.19, 133.82, 130.19, 127.85, 125.77, 65.88, 20.50. EI-MS: m/z 212.
2-(2-chlorophenyl)-2-oxoethyl acetate (2o)

Yellow oil (78%, 33.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63-7.60 (m, 1 H), 7.45-7.43 (m, 2 H), 7.38-7.34 (m, 1 H), 5.20 (s, 2 H), 2.18 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.25, 170.29, 135.77, 132.76, 131.53, 130.54, 129.93, 127.08, 68.23, 20.38. EI-MS: m/z 212.

2-(3,4-dichlorophenyl)-2-oxoethyl acetate (2p)

White solid (80%, 39.3 mg), melting point: 68–70 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00-7.99 (m, 1 H), 7.75-7.72 (m, 1 H), 7.59-7.57 (m, 1 H), 5.27 (s, 2 H), 2.23 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.23, 170.26, 138.53, 133.64, 133.59, 130.99, 129.74, 126.69, 65.72, 20.44. EI-MS: m/z 246.

2-(4-fluorophenyl)-2-oxoethyl acetate (2q)$^6$

White solid (87%, 34.1 mg), melting point: 48–50 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98-7.92 (m, 2 H), 7.19-7.14 (m, 2 H), 5.30 (s, 2 H), 2.23 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.63, 170.33, 167.36-164.81 (d, $J = 255$ Hz), 130.48, 130.39, 116.17-115.96 (d, $J = 21$ Hz), 65.76, 20.49. EI-MS: m/z 196.

2-(4-bromophenyl)-2-oxoethyl acetate (2r)$^5$


2-(3-bromophenyl)-2-oxoethyl acetate (2s)

White solid (78%, 40.0 mg), melting point: 60–62 °C.

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 8.04 (m, 1 H), 7.84-7.82 (m, 1 H), 7.75-7.73 (m, 1 H), 7.40-7.36 (m, 1 H), 5.30 (s, 2 H), 2.23 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 190.95, 170.31, 136.71, 135.72, 130.77, 130.41, 126.19, 123.13, 65.83, 20.49. EI-MS: m/z 256.

2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl acetate (2t)

White solid (57%, 28.0 mg), melting point: 76–78 °C.

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 8.04-8.02 (d, \(J=8.0\) Hz, 2 H), 7.77-7.75 (d, \(J=8.0\) Hz, 2 H), 5.34 (s, 2 H), 2.24 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 191.46, 170.31, 136.83, 135.59-134.62 (q, \(J=32\) Hz), 128.15, 125.98-125.87 (q, \(J=4\) Hz), 127.43-119.30 (q, \(J=271\) Hz), 65.99, 20.45. EI-MS: m/z 246.

2-(4-nitrophenyl)-2-oxoethyl acetate (2u)

White solid (95%, 48.6 mg), melting point: 72–74 °C.

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 7.79-7.76 (m, 2 H), 7.65-7.61 (m, 2 H), 5.29 (s, 2 H), 2.22 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 191.25, 170.32, 132.78, 132.15, 129.17, 129.08, 65.77, 20.47. EI-MS: m/z 256.
White Solide (49%, 21.8 mg), melting point: 118−120 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36-8.33 (m, 2 H), 8.10-8.06 (m, 2 H), 5.34 (s, 2 H), 2.24 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.08, 170.25, 150.73, 138.65, 128.90, 124.07, 66.04, 20.41. EI-MS: m/z 223.

1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl acetate (2v)$^5$

White solide (91%, 37.1 mg), melting point: 74–76 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03-8.01 (m, 1 H), 7.52-7.48 (m, 1 H), 7.35-7.25 (m, 2 H), 5.57 (m, 1 H), 3.25-3.17 (m, 1 H), 3.11-3.05 (m, 1 H), 2.43-2.36 (m, 1 H), 2.34-2.26 (m, 1 H), 2.22 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.90, 170.13, 143.01, 133.85, 131.51, 128.58, 127.75, 126.90, 74.52, 29.08, 27.89, 20.80. EI-MS: m/z 204.

2-oxocyclohexyl acetate (2w)$^5$

Colorless oil (33%, 10.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.19-5.14 (m, 1 H), 2.55-2.49 (m, 1 H), 2.44-2.35 (m, 1 H), 2.33-2.27 (m, 1 H), 2.16 (s, 3 H), 2.14-2.06 (m, 1 H), 2.02-1.93 (m, 1 H), 1.80-1.74 (m, 2 H), 1.68-1.60 (m, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.51, 170.01, 76.53, 40.67, 33.05, 27.13, 23.75, 20.70. EI-MS: m/z 156.
2-(furan-2-yl)-2-oxoethyl acetate (2y)\textsuperscript{10}

Colorless oil (30\%, 10.1 mg). $^1$H NMR (400 MHz, CDCl\textsubscript{3})

$\delta$ 7.62-7.61 (m, 1 H), 7.29-7.28 (d, $J = 3.6$ Hz, 1 H), 6.59-6.58 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1 H), 5.19 (s, 2 H), 2.22 (s, 3 H).

$^1$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 181.69, 170.34, 150.53, 146.75, 117.73, 112.49, 65.33, 20.50. EI-MS: m/z 168.

2-oxo-2-(thiophen-2-yl)ethyl acetate (2z)\textsuperscript{10}

Colorless oil (54\%, 19.9 mg). $^1$H NMR (400 MHz, CDCl\textsubscript{3})

$\delta$ 7.77-7.76 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.2$ Hz, 1 H), 7.72-7.71 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.2$ Hz, 1 H), 7.18-7.16 (dd, $J_1 = 4.8$ Hz, $J_2 = 4.0$ Hz, 1 H), 5.23 (s, 2 H), 2.23 (s, 3 H).

$^1$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 185.37, 170.31, 140.28, 134.32, 131.94, 128.25, 65.69, 20.51. EI-MS: m/z 184.

2-oxo-2-(pyridin-2-yl)ethyl acetate (2aa)\textsuperscript{11}

Colorless oil (77\%, 27.6 mg). $^1$H NMR (400 MHz, CDCl\textsubscript{3})

$\delta$ 8.66-8.65 (m, 1 H), 8.04-8.02 (m, 1 H), 7.88-7.84 (m, 1 H), 7.53-7.50 (m, 1 H), 5.62 (s, 2 H), 2.24 (s, 3 H).

$^1$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 193.42, 170.47, 151.52, 149.02, 137.00, 127.84, 121.83, 66.82, 20.56. EI-MS: m/z 179.
1-oxo-1-phenylpropan-2-yl acetate (2ab)$^5$

Colorless oil (94%, 36.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96-7.93 (m, 2 H), 7.61-7.57 (m, 1 H), 7.50-7.46 (m, 2 H), 6.00-5.94 (q, $J = 7.2$ Hz, 1 H), 2.15 (s, 3 H), 1.54-1.52 (d, $J = 7.2$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.82, 170.36, 134.27, 133.53, 128.72, 128.38, 71.35, 20.68, 17.09. EI-MS: m/z 192.

2-methyl-1-oxo-1-phenylpropan-2-yl acetate (2ac)$^{12}$

Colorless oil (98%, 40.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02-8.00 (m, 2 H), 7.51-7.48 (m, 1 H), 7.42-7.38 (m, 2 H), 1.93 (s, 3 H), 1.72 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.07, 170.03, 134.56, 132.38, 128.38, 128.31, 84.20, 25.29, 21.31. EI-MS: m/z 206.

2-oxo-2-phenylethyl propionate (2ad)$^7$

Colorless oil (84%, 32.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92-7.90 (m, 2 H), 7.63-7.59 (t, $J = 7.6$ Hz, 1 H), 7.51-7.47 (t, $J = 7.6$ Hz, 2 H), 5.35 (s, 2 H), 2.56-2.50 (q, $J = 7.6$ Hz, 2 H), 1.24-1.20 (d, $J = 7.6$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 192.29, 173.88, 134.15, 133.81, 128.79, 127.69, 65.82, 27.17, 9.00. EI-MS: m/z 192.
2-oxo-2-phenylethyl isobutyrate (2ae)\textsuperscript{13}

Colorless oil (86%, 35.4 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.92-7.90 (m, 2 H), 7.62-7.58 (m, 1 H), 7.50-7.46 (m, 2 H), 5.34 (s, 2 H), 2.80-2.69 (m, 1 H), 1.28 (s, 3 H), 1.26 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 192.34, 176.53, 134.20, 133.76, 128.78, 127.68, 65.72, 33.74, 18.93. EI-MS: m/z 206.

2-oxo-2-phenylethyl benzoate (2af)\textsuperscript{7}

White Solide (66%, 31.7 mg), melting point: 104-106 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.15-8.13 (m, 2 H), 7.98-7.95 (m, 2 H), 7.64-7.57 (m, 2 H), 7.52-7.45 (m, 4 H), 5.58 (s, 2 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 192.07, 166.01, 134.26, 133.86, 133.32, 129.94, 129.37, 128.86, 128.41, 127.80, 66.42. EI-MS: m/z 240.

2-hydroxy-1-phenylethan-1-one (3a)\textsuperscript{14}

White solide (19%, 5.2 mg), melting point: 54–56 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.94-7.92 (m, 2 H), 7.66-7.62 (m, 1 H), 7.53-7.49 (m, 2 H), 4.89-4.88 (d, \(J = 4.8\) Hz, 2 H), 3.52-3.50 (t, \(J = 4.8\) Hz, 1 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 198.38, 134.29, 133.38, 128.97, 127.68, 65.45. EI-MS: m/z 136.


2aa
2ac
2ac
2a

$2a : dS-2a = 2 : 1$