Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Catalytic transformation of esters of 1,2-azido alcohols into α-amido ketones

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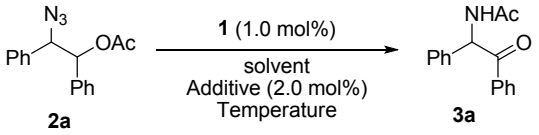
Contents

1. General Information

Air-sensitive manipulations were carried out with standard Schlenk techniques under argon atmosphere. Commercial chemicals used without further purification. All ionic liquids were dried and degassed at 100 ^{o}C for 1 h under high vacuum prior to experiments. Flash column chromatography was carried out on silica gel (230-400 mesh) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AVANCE III 300MHZ FT-NMR spectrometer and chemical shift are given in δ ppm. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS, 0 ppm). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.23 ppm) as an internal standard. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer with NaCl pellet. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Ruthinum complex **1** was synthesized according to the literature procedure.[1]

2. Optimization (Effect of ionic liquids and additives)

Table 1. Transformation of **2a** to **3a** under various ionic liquids and additives.[a]



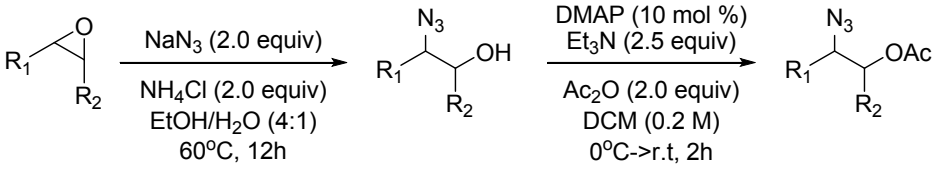
2a **3a**

Entry	Solvent	Additive	Temp. (^{o}C)	Yield (%)[b]
1	[bmim]Cl	Et_3N	70	96
2	[bmim]BF_4	Et_3N	70	n.d
3	[bmim]PF_6	Et_3N	70	n.d
4	[hmim]Cl	Et_3N	70	92
5	[omim]Cl	Et_3N	70	68
6	[bmim]Cl	DBU	70	22
7	[bmim]Cl	pyridine	50	85
8	[bmim]Cl	DIEPA	70	65

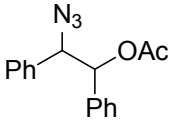
[a] Typical reaction conditions a solution of an azide (0.25 mmol), **1** (1.0 mol%) additives and (2.0 mol%) in a solvent (1.0 mL) was stirred for 12 h. [b] Estimated by ^{1}H NMR using nitromethane as an internal standard.

3. Synthesis of Substrates

3-a. Synthesis of 1,2-azido acetates (2a~2d, 2j, 2t~2w)

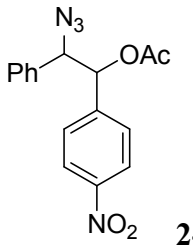


A solution of epoxide (3.0 mmol), ammonium chloride (2.0 equiv, 6.0 mmol) and sodium azide (2.0 equiv, 6.0 mmol) in a mixture of ethanol and water (4:1, 20 mL, 0.15 M) was stirred for 12 h at 60 °C. After completion of the reaction, the mixture was extracted with ethyl acetate (3 x 30 mL). The oragnic layer was washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. To a solution of the crude 1,2-azido alcohol, *N,N*-dimethylaminopyridine (10 mol%, 0.3 mmol) and triethylamine (2.5 equiv, 7.5 mmol) in dichloromethane (20 mL, 0.2 M), acetic anhydride (2.0 equiv, 6.0 mmol) was added at 0 °C. The reaction mixture was stirred for 2 h, and extracted with dichloromethane (3 x 20 mL). The organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the corresponding 1,2-azido acetate.



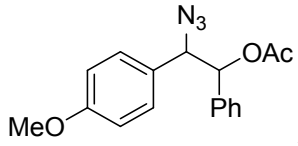
2-azido-1,2-diphenylethyl acetate (2a)

Yield: 87% (2 steps); Colorless gum; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.28 (m, 6H), 7.25-7.18 (m, 4H), 5.94 (d, *J* = 6.5 Hz, 1H), 4.89 (d, *J* = 6.5 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.6, 136.2, 135.8, 128.8, 128.7, 128.4, 128.0, 127.9, 69.2, 21.1; IR(NaCl): ν = 3090, 3066, 3034, 2107, 1747, 1604, 1587, 1496, 1455, 1372 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{16}H_{16}N_3O_2$ $[M + H]^+$: 282.1240; found: 282.1243.



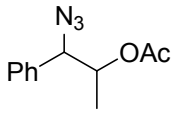
2-azido-1-(4-nitrophenyl)-2-phenylethyl acetate (2b)

Yield: 77% (2 steps); Pale yellow gum; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.15-8.12 (m, 2H), 7.35-7.31 (m, 5H), 7.18-7.15 (m, 2H), 5.98 (d, *J* = 5.8 Hz, 1H), 4.98 (d, *J* = 5.8 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.5, 148.0, 143.0, 134.8, 129.1, 128.9, 128.8, 127.7, 123.3, 76.9, 68.5, 20.9; IR(NaCl): ν = 3112, 3065, 2106, 1751, 1608, 1539, 1348 cm^{-1}; HRMS (EI): m/z calcd. for $C_{16}H_{15}N_4O_4$ $[M + H]^+$: 327.1093; found: 327.1097.



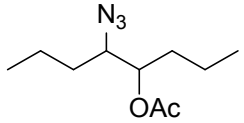
2-azido-2-(4-methoxyphenyl)-1-phenylethyl acetate (2c)

Yield: 78% (2 steps); Colorless gum; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.27-7.08 (m, 5H), 7.00-6.97 (m, 2H), 6.76-6.73 (m, 2H), 5.89 (d, *J* = 8.6 Hz, 1H), 4.74 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.9, 159.8, 136.9, 129.2, 128.6, 128.4, 127.5, 114.1, 113.5, 78.7, 69.4, 55.4, 21.3; IR(NaCl): ν = 3035, 2961, 2106, 1745, 1613, 1515, 1345 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{17}H_{17}O_3$ $[M - N_3]^+$: 269.1172; found: 269.1176.



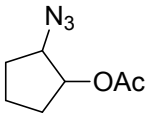
1-azido-1-phenylpropan-2-yl acetate (2d)

Yield: 85% (2 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.32 (m, 5H), 5.18-5.10 (m, 1H), 4.74 (d, *J* = 4.7 Hz, 1H), 2.04 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.4, 136.1, 128.8, 128.6, 127.5, 73.2, 68.5, 21.3, 14.8; IR(NaCl): ν = 3065, 2989, 2940, 2104, 1740, 1604, 1586, 1494, 1372 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{11}H_{14}N_3O_2$ $[M + H]^+$: 220.1086; found: 220.1084.



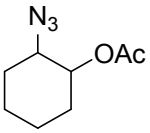
5-azidooctan-4-yl acetate (2j)

Yield: 91% (2 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.92-4.86 (m, 1H), 3.43-3.38 (m, 1H), 2.00 (s, 3H), 1.66-1.17 (m, 8H), 0.90-0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.3, 75.4, 64.7, 32.2, 31.1, 20.7, 19.7, 18.7, 13.7, 13.6; IR(NaCl): ν = 2962, 2938, 2876, 2115, 1744, 1367, 1374 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{11}H_{20}N_3O_2$ $[M + H]^+$: 214.1559; found: 214.1556.



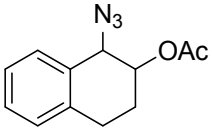
2-azidocyclopentyl acetate (2t)[2]

Yield: 83% (2 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.93-4.90 (m, 1H), 3.85-3.80 (m, 1H), 2.09-1.92 (m, 2H), 2.00 (s, 3H, overlap), 1.77-1.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.4, 79.5, 66.3, 30.0, 29.4, 21.3, 21.1.



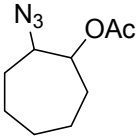
2-azidocyclohexyl acetate (2u)[3]

Yield: 94% (2 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.72-4.64 (m, 1H), 3.42-3.34 (m, 1H), 2.09 (s, 3H, overlap), 2.08-2.03 (m, 2H), 1.76-1.73 (m, 2H), 1.38-1.28 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.5, 75.7, 63.4, 30.8, 30.6, 24.0, 23.7, 21.4.



1-azido-1,2,3,4-tetrahydronaphthalen-2-yl acetate (2v)

Yield: 95% (2 steps); Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.36 (m, 1H), 7.27-7.24 (m, 2H), 7.16-7.13 (m, 1H), 5.18-5.12 (m, 1H), 4.59 (d, J = 6.4 Hz, 1H), 2.93-2.89 (m, 2H), 2.25-2.15 (m, 1H), 2.09 (s, 3H), 2.03-1.93 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.5, 136.2, 131.9, 129.2, 129.1, 128.5, 126.8, 72.8, 62.5, 26.0, 25.4, 21.4; IR(NaCl): ν = 3065, 3024, 2939, 2847, 2100, 1740, 1606, 1507, 1491, 1437, 1369 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{12}H_{14}N_3O_2$ $[M + H]^+$: 232.1086; found: 232.1089.

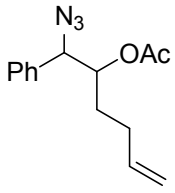


2-azidocycloheptyl acetate (2w)

Yield: 82% (2 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.86-4.79 (m, 1H), 3.61-3.55 (m, 1H), 2.09 (s, 3H), 1.91-1.76 (m, 2H), 1.74-1.62 (m, 4H), 1.60-1.47 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.4, 78.7, 66.5, 31.1, 30.2, 27.9, 23.6, 22.6, 21.5; IR(NaCl): ν = 2937, 2864, 2098, 1739, 1458, 1447, 1372 cm^{-1}; HRMS (FAB): m/z calcd. for $C_9H_{16}N_3O_2$ $[M + H]^+$: 198.1243; found: 198.1245.

3-b. Synthesis of 1,2-azido acetates (2e)

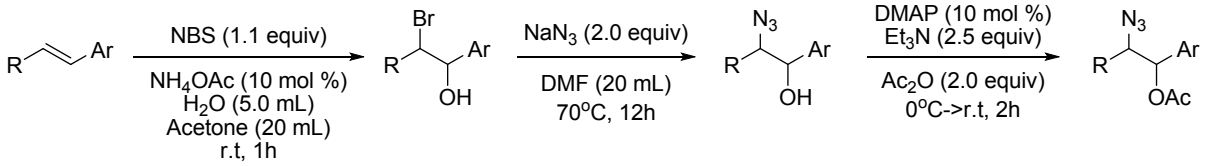
1-Azido-1-phenylhex-5-en-2-ol was synthesized according to the literature procedure.[4] To a solution of the 1,2-azido alcohol (3.0 mmol), *N,N*-dimethylaminopyridine (10 mol %, 0.3 mmol) and triethylamine (2.5 equiv, 7.5 mmol) in dichloromethane (20 mL, 0.15 M), acetic anhydride (2.0 equiv, 6.0 mmol) was added at 0 °C. The reaction mixture was stirred for 2 h, and extracted with dichloromethane (3 x 20 mL). The organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the 1,2-azido acetate **2e**.



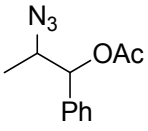
1-azido-1-phenylhex-5-en-2-yl acetate (2e)

Yield: 94%; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41-7.28 (m, 5H), 5.74-5.61 (m, 1H), 5.22-5.15 (m, 1H), 4.98-4.90 (m, 2H), 4.54 (d, *J* = 7.4 Hz, 1H), 2.09 (s, 3H), 2.05-1.94 (m, 2H), 1.59-1.49 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.4, 137.2, 136.1, 129.0, 128.9, 127.8, 115.4, 74.9, 68.4, 30.4, 29.4, 21.0; IR(NaCl): ν = 3066, 3033, 2978, 2958, 2924, 2101, 1744, 1642, 1494, 1455, 1373 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{14}H_{17}O_2$ $[M - N_3]^+$: 217.1223; found: 217.1217.

3-c. Synthesis of 1,2-azido acetates (2f~2i)



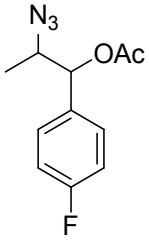
To a suspension of an olefin (5.0 mmol) and NH_4OAc (10 mol%, 0.5 mmol) in acetone (20 mL, 0.25 M), *N*-bromosuccinimide (1.1 equiv, 5.5 mmol) and water (5.0 ml) were added, and the reaction mixture was stirred at room temperature for 1 h.[5] After completion of the reaction as indicated by TLC, the mixture was concentrated in vaco and extracted with EtOAc-H_2O (1:1) (3 × 30 mL). The organic layer was concentrated under reduced pressure. The bromohydrin was used without further purification. To a solution of the bromohydrin in DMF (20 mL), NaN_3 (2.0 equiv) was added and the reaction mixtrue was stirred at 70 °C for 12 h. After completion of the reaction as indicated by TLC, the mixture was extracted with diethyl ether (3 x 20 mL), washed with H_2O (50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure to give crude 1,2-azido alcohol. To a solution of the crude 1,2-azido alcohol, *N,N*-dimethylaminopyridine (10 mol%) and triethylamine (2.5 equiv) in dichloromethane (0.2 M) acetic anhydride (2.0 equiv) was added at 0 °C. The reaction mixture was stirred for 2 h, and extracted with dichloromethane (3 x 20 mL). The organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the 1,2-azido acetate.



2-azido-1-phenylpropyl acetate (2f)

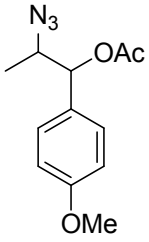
Yield: 62% (3 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.30 (m, 5H), 5.64 (d, *J* = 7.6 Hz, 1H), 3.84-3.75 (m, 1H), 2.13 (s, 3H), 1.08 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.0, 137.4, 128.9, 128.8, 127.4, 79.1, 60.9, 21.2, 16.4; IR(NaCl): ν =

3090, 3066, 3035, 2983, 2938, 2110, 1744, 1605, 1587, 1494, 1372 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{11}H_{13}N_3O_2$ $[M + H]^+$: 220.1086; found: 220.1085.



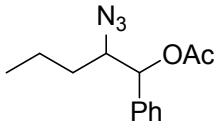
2-azido-1-(4-fluorophenyl)propyl acetate (2g)

Yield: 65% (3 steps); Pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.32 (m, 2H), 7.11-7.05 (m, 2H), 5.64 (d, *J* = 7.4 Hz, 1H), 3.83-3.74 (m, 1H), 2.15 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.9, 164.6, 161.3, 133.3, 133.2, 129.3, 129.2, 129.1, 116.0, 115.7, 78.4, 60.8, 21.2, 16.3; IR(NaCl): ν = 3119, 3075, 3052, 2985, 2940, 2108, 1751, 1696, 1653, 1608, 1513, 1375 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{11}H_{13}FN_3O_2$ $[M + H]^+$: 238.0992; found: 238.0989.



2-azido-1-(4-methoxyphenyl)propyl acetate (2h)[6]

Yield: 63% (3 steps); Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.28-7.25 (m, 2H), 6.90-6.87 (m, 2H), 5.59 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H, overlap), 3.80-3.76 (m, 1H, overlap), 2.11 (s, 3H), 1.06 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.1, 160.0, 129.5, 128.7, 114.2, 78.9, 60.9, 55.5, 21.3, 16.4.

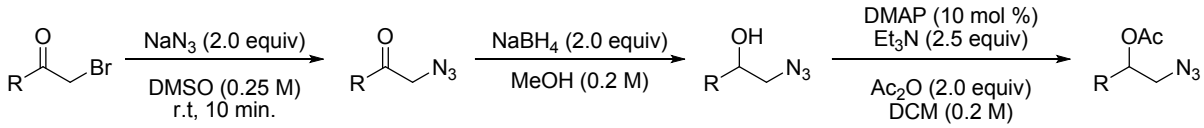


2-azido-1-phenylpentyl acetate (2i)

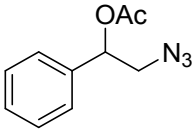
Yield: 71% (3 steps); Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.40-7.32 (m, 5H), 5.71 (d, *J* = 7.4 Hz, 1H), 3.69-3.57 (m, 1H), 2.13 (s, 3H), 1.57-1.45 (m, 1H), 1.39-1.21 (m, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.0, 137.6, 128.9, 127.3, 78.5, 66.0, 32.8, 21.2, 19.5, 13.8; IR(NaCl): ν = 3066, 3035, 2961, 2875, 2112, 1745, 1696, 1685,

1653, 1507, 1457, 1373 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{13}H_{18}N_3O_2$ $[M + H]^+$: 248.1399; found: 248.1403.

3-d. Synthesis of 1,2-azido acetates (2k~2s)



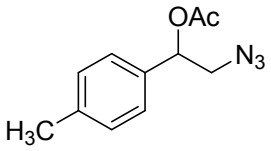
To a solution of an α-bromo ketone (5.0 mmol) in dimethylsulfoxide (20 mL, 0.25 M) was added NaN_3 (2.0 equiv, 10 mmol) and stirred at room temperature for 10 min. After completion of the reaction as indicated by TLC, the mixture was extracted with diethyl ether (3 x 20 mL), washed with H_2O (50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. To a solution of the crude α-azido ketone in MeOH (0.2 M) was added $NaBH_4$ (2.0 equiv) and stirred at room temperature for 1 h. After completion of the reaction as indicated by TLC, the mixture was extracted with dichloromethane (3 x 20 mL), washed with H_2O (40 mL) and brine (40 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. To a solution of the crude 1,2-azido alcohol, *N,N*-dimethylaminopyridine (10 mol%) and triethylamine (2.5 equiv) in dichloromethane (0.2 M) acetic anhydride (2.0 equiv) was added at 0 °C. The reaction mixture was stirred for 2 h, and extracted with dichloromethane (3 x 20 mL). The organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the 1,2-azido acetate.



2-azido-1-phenylethyl acetate (2k)[7]

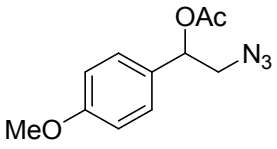
Yield: 56% (3 steps); Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.41-7.30 (m, 5H), 5.92 (dd, *J* = 8.1, 4.0 Hz, 1H), 3.63 (dd, *J* = 13.1, 8.1 Hz, 1H), 3.43 (dd, *J* = 13.1, 3.9 Hz, 1H),

2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.1, 137.3, 129.0, 128.9, 126.6, 74.8, 55.3, 21.3.



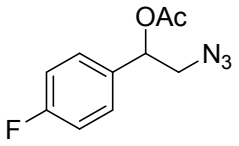
2-azido-1-p-tolylethyl acetate (2l) [7]

Yield: 85% (3 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.25-7.22 (m, 2H), 7.18-7.15 (m, 2H), 5.88 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.61 (dd, *J* = 13.0, 8.1 Hz, 1H), 3.39 (dd, *J* = 13.1, 3.9 Hz, 1H), 2.33 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.0, 138.7, 134.4, 129.5, 126.5, 74.6, 55.2, 21.3, 21.2.



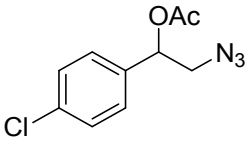
2-azido-1-(4-methoxyphenyl)ethyl acetate (2m) [7]

Yield: 62% (3 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.30-7.26 (m, 2H), 6.91-6.88 (m, 2H), 5.87 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.80 (s, 3H), 3.62 (dd, *J* = 13.1, 8.2 Hz, 1H), 3.40 (dd, *J* = 13.1, 4.1 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.1, 160.1, 129.4, 128.1, 114.3, 74.5, 55.5, 55.2, 21.3.



2-azido-1-(4-fluorophenyl)ethyl acetate (2n)[8]

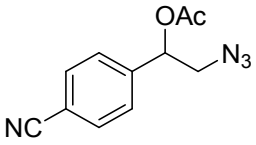
Yield: 85% (3 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.31 (m, 2H), 7.08-7.03 (m, 2H), 5.89 (dd, *J* = 7.9, 4.1 Hz, 1H), 3.60 (dd, *J* = 13.1, 7.9 Hz, 1H), 3.41 (dd, *J* = 13.1, 4.1 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.9, 164.5, 161.2, 133.2, 133.1, 128.5, 128.4, 116.0, 115.7, 74.0, 55.1, 21.1.



2-azido-1-(4-chlorophenyl)ethyl acetate (2o) [8]

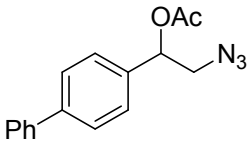
Yield: 75% (3 steps); Pale ellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37-7.33 (m, 2H), 7.31-7.26 (m, 2H), 5.87 (dd, *J* = 7.8, 4.1 Hz, 1H), 3.60 (dd, *J* = 13.1, 7.8 Hz, 1H), 3.42 (dd, *J*

= 13.1, 4.0 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.9, 135.8, 134.8, 129.1, 128.1, 74.1, 55.1, 21.2.



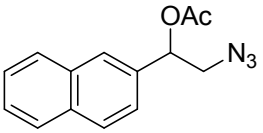
2-azido-1-(4-cyanophenyl)ethyl acetate (2p) [7]

Yield: 72% (3 steps); White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.69-7.67 (m, 2H), 7.50-7.47 (m, 2H), 5.93 (dd, *J* = 7.3, 4.2 Hz, 1H), 3.62 (dd, *J* = 13.2, 7.3 Hz, 1H), 3.50 (dd, *J* = 13.2, 4.2 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.7, 142.3, 132.6, 127.2, 118.4, 112.6, 73.8, 54.7, 20.9.



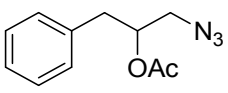
2-azido-1-(biphenyl-4-yl)ethyl acetate (2q)

Yield: 73% (3 steps); Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.59-7.51 (m, 4H), 7.44-7.29 (m, 5H), 5.95 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.63 (dd, *J* = 13.1, 8.2 Hz, 1H), 3.42 (dd, *J* = 13.2, 4.0 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.0, 141.7, 140.5, 136.2, 128.9, 127.7, 127.6, 127.2, 127.0, 74.5, 55.1, 21.1; IR(NaCl): ν = 3057, 3031, 2930, 2103, 1747, 1614, 1524, 1373 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{16}H_{15}N_3O_2$: 281.1164; found: 281.1166.



2-azido-1-(naphthalen-2-yl)ethyl acetate (2r)[9]

Yield: 67% (3 steps); Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.86-7.82 (m, 4H), 7.51-7.42 (m, 3H), 6.08 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.72 (dd, *J* = 13.1, 8.1 Hz, 1H), 3.50 (dd, *J* = 13.1, 3.9 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.1, 134.6, 133.5, 133.3, 128.9, 128.2, 127.9, 126.7, 126.1, 124.0, 74.9, 55.2, 21.3

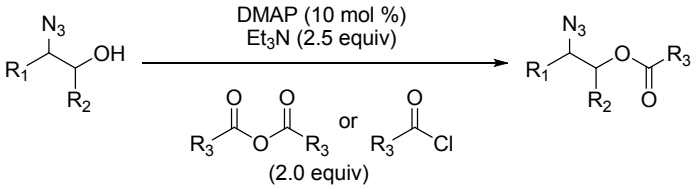


1-azido-3-phenylpropan-2-yl acetate (2s) [9]

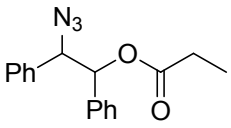
Yield: 81% (2 steps); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.32-7.18 (m, 5H), 5.23-5.13 (m, 1H), 3.38 (dd, *J* = 13.1, 3.6 Hz, 1H), 3.25 (dd, *J* = 13.1, 5.8 Hz, 1H), 2.97 (dd, *J* =

13.7, 6.5 Hz, 1H), 2.87(dd, J = 13.7, 7.4 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.3, 136.3, 129.5, 128.7, 127.0, 73.5, 52.5, 37.7, 21.1.

3-e. Synthesis of various esters of 1,2-azido alcohols (4a~4j)

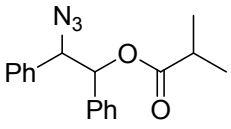


To a solution of 1,2-azido alcohol (3.0 mmol), *N,N*-dimethylaminopyridine (10 mol%, 0.3 mmol) and triethylamine (2.5 equiv, 7.5 mmol) in dichloromethane (15 mL, 0.2 M) acid anhydride (or acid chloride) (2.0 equiv) was added at 0 °C. The reaction mixture was stirred for 2 h, and extracted with dichloromethane (3 x 20 mL). The organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the 1,2-azido ester.



2-azido-1,2-diphenylethyl propionate (4a)

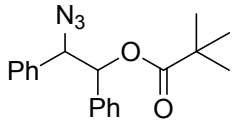
Yield: 99%; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.30 (m, 6H), 7.24-7.19 (m, 4H), 5.96 (d, J = 6.6 Hz, 1H), 4.89 (d, J = 6.6 Hz, 1H), 2.27 (q, J = 7.5 Hz, 2H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 173.0, 136.4, 135.8, 128.8, 128.6, 128.4, 128.0, 127.9, 77.4, 69.3, 27.8, 9.1; IR(NaCl): ν = 3065, 3034, 2107, 1724, 1602, 1585, 1496, 1452, 1316 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{17}H_{18}N_3O_2$ $[M + H]^+$: 296.1399; found: 296.1403.



2-azido-1,2-diphenylethyl isobutyrate (4b)

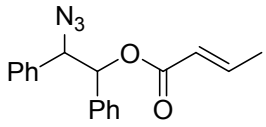
Yield: 92%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34-7.29 (m, 6H), 7.25-7.21 (m, 4H), 5.94 (d, J = 6.9 Hz, 1H), 4.86 (d, J = 6.9 Hz, 1H), 2.52-2.43 (m, 1H), 1.04 (d, J = 7.0 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.5, 136.6, 135.9, 128.8,

128.7, 128.6, 128.4, 128.0, 127.8, 77.1, 69.4, 34.2, 18.83, 18.80; IR(NaCl): ν = 3066, 3034, 2976, 2935, 2876, 2106, 1741, 1587, 1498, 1469, 1455, 1388 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{18}H_{20}N_3O_2$ $[M + H]^+$: 310.1556; found: 310.1554.



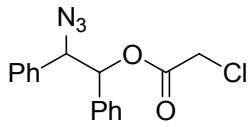
2-azido-1,2-diphenylethyl pivalate (4c)

Yield: 62%; White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.32-7.28 (m, 6H), 7.25-7.21 (m, 4H), 5.91 (d, *J* = 7.0 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.8, 136.8, 136.0, 128.8, 128.7, 128.6, 128.4, 128.0, 127.6, 69.6, 38.9, 27.0; IR(NaCl): ν = 3110, 3066, 3035, 2974, 2935, 2906, 2105, 1736, 1621, 1605, 1588, 1497, 1480, 1455, 1397, 1365 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{22}N_3O_2$ $[M + H]^+$: 324.1712; found: 324.1708.



2-azido-1,2-diphenylethyl but-2-enoate (4d)

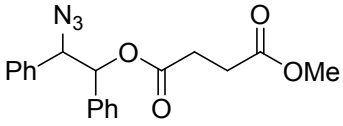
Yield: 85%; White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.30-7.23 (m, 6H), 7.22-7.16 (m, 4H), 7.02-6.90 (m, 1H), 6.00 (d, *J* = 6.0 Hz, 1H), 5.83 (dq, *J* = 15.5, 1.6 Hz, 1H), 4.95 (d, *J* = 6.0 Hz, 1H), 1.84 (dd, *J* = 6.9, 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.0, 146.1, 136.2, 135.6, 128.7, 128.6, 128.5, 128.2, 127.9, 127.8, 122.3, 77.5, 69.2, 18.2; IR(NaCl): ν = 3090, 3065, 3034, 2972, 2944, 2915, 2106, 1725, 1657, 1604, 1587, 1497, 1455, 1443, 1376 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{18}H_{18}N_3O_2$ $[M + H]^+$: 308.1399; found: 308.1397.



2-azido-1,2-diphenylethyl 2-chloroacetate (4e)

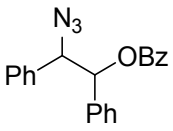
Yield: 95%; Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.32-7.29 (m, 6H), 7.26-7.19 (m, 4H), 5.97 (d, *J* = 6.7 Hz, 1H), 4.90 (d, *J* = 6.7 Hz, 1H), 3.92 (d, *J* = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.9, 135.4, 135.2, 129.1, 129.0, 128.7, 128.5, 128.0, 127.8, 79.1, 68.9, 40.8; IR(NaCl): ν = 3090, 3066, 3034, 2954, 2900, 2500, 2107, 1764, 1604, 1587, 1496,

1455, 1348 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{16}H_{14}ClO_2$ $[M - N_3]^+$: 273.0677; found: 273.0685.



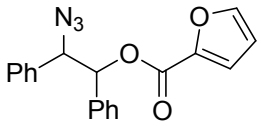
2-azido-1,2-diphenylethyl methyl succinate (4f)

Yield: 80%; White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 6H), 7.20-7.18 (m, 4H), 5.95 (d, *J* = 6.3 Hz, 1H), 4.91 (d, *J* = 6.3 Hz, 1H), 3.62 (s, 3H), 2.63-2.51 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.5, 170.9, 136.0, 135.7, 128.9, 128.8, 128.7, 128.4, 128.0, 127.9, 78.0, 69.1, 52.0, 29.4, 29.0; IR(NaCl): ν = 3034, 2953, 2107, 1739, 1701, 1655, 1496, 1455, 1437 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{20}N_3O_4$ $[M + H]^+$: 354.1454; found: 354.1450.



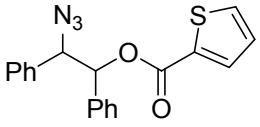
2-azido-1,2-diphenylethyl benzoate (4g)

Yield: 84%; White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.03-7.99 (m, 2H), 7.57-7.51 (m, 1H), 7.44-7.39 (m, 2H), 7.35-7.22 (m, 10H) 6.19 (d, *J* = 5.9 Hz, 1H), 5.08 (d, *J* = 5.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.3, 136.1, 135.6, 133.5, 129.9, 129.8, 128.8, 128.7, 128.6, 128.4, 128.0, 127.8, 78.4, 69.4; IR(NaCl): ν = 3065, 3034, 2107, 1724, 1602, 1585, 1496, 1452, 1347 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{21}H_{18}N_3O_2$ $[M + H]^+$: 347.1399; found: 347.1397.



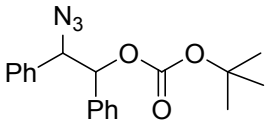
2-azido-1,2-diphenylethyl furan-2-carboxylate (4h)

Yield: 95%; White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.55-7.54 (m, 1H), 7.32-7.18 (m, 11H), 6.47-6.45 (m, 1H), 6.16 (d, *J* = 5.8 Hz, 1H), 5.04 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.2, 147.0, 144.2, 135.7, 135.3, 128.8, 128.7, 128.6, 128.3, 128.0, 127.8, 118.8, 112.1, 78.1, 69.1; IR(NaCl): ν = 3210, 3066, 3034, 2106, 1727, 1604, 1579, 1568, 1497, 1471, 1455, 1395 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{16}N_3O_3$ $[M + H]^+$: 334.1192; found: 334.1190.



2-azido-1,2-diphenylethyl thiophene-2-carboxylate (4i)

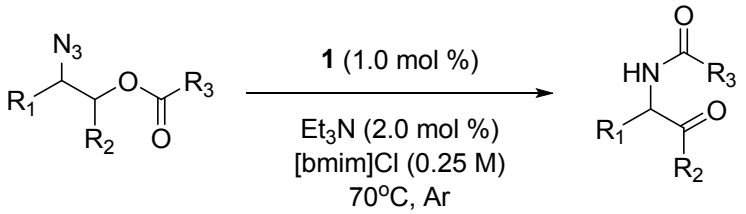
Yield: 98%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ =7.79-7.78 (m, 1H), 7.54-7.52 (m, 1H), 7.31-7.21 (m, 10H), 7.07-7.04 (m, 1H), 6.13 (d, *J* = 5.8 Hz, 1H), 5.04 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.5, 137.7, 137.2, 135.9, 135.0, 134.9, 130.6, 130.5, 130.4, 130.1, 129.8, 129.5, 80.2, 71.1; IR(NaCl): ν = 3108, 3091, 3065, 3033, 2106, 1715, 1524, 1496, 1454, 1416, 1360 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{16}N_3O_2S$ $[M + H]^+$: 350.0963; found: 350.0966.



2-azido-1,2-diphenylethyl tert-butyl carbonate (4j)

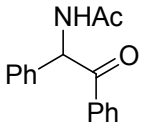
Yield: 90%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34-7.24 (m, 10H), 5.71 (d, *J* = 6.9 Hz, 1H), 4.89 (d, *J* = 6.9 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.4, 136.2, 135.8, 128.9, 128.8, 128.7, 128.4, 128.2, 127.9, 82.9, 80.1, 69.2, 27.8; IR(NaCl): ν = 3091, 3066, 3034, 2982, 2934, 2106, 1745, 1605, 1589, 1495, 1455, 1395, 1370 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{22}N_3O_3$ $[M + H]^+$: 340.1661; found: 340.1665.

4. Synthesis of α-amido ketones



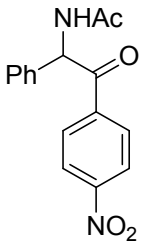
1-Butyl-3-methylimidazolium chloride ([bmim]Cl) (1.0 mL) was added to a flame-dried J-young flask then stirred at 100°C for 1h. The ruthenium catalyst **1** (1.0 mol%), the substrate (0.25 mmol) and triethylamine (2.0 mol%) was added under stream of argon flow and stirred at 70 °C for 12 h. After completion of the reaction, the reaction mixture was cool down to room temperature then dilluted with H_2O (5.0 mL) and extracted with dichloromethane (3 x 5

mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the corresponding α-amiodo ketone.



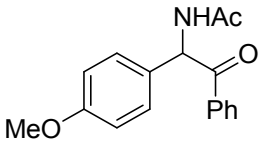
***N*-(2-oxo-1,2-diphenylethyl)acetamide (3a)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98-7.95 (m, 2H), 7.54-7.48 (m, 1H), 7.42-7.37 (m, 4H), 7.30-7.22 (m, 3H), 7.02 (d, *J* = 6.9 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.1, 169.4, 137.5, 134.5, 134.0, 129.4, 129.3, 128.9, 128.6, 128.4, 58.6, 23.5; IR(NaCl): ν = 3287, 3062, 1692, 1653, 1597, 1531, 1448, 1372 cm^{-1}; HRMS (EI): m/z calcd. for $C_{16}H_{15}NO_2$: 253.1103; found: 253.1101.



***N*-(2-(4-nitrophenyl)-2-oxo-1-phenylethyl)acetamide (3b)**

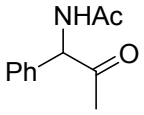
Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.38-7.26 (m, 5H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.57 (d, *J* = 7.1 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.8, 169.6, 150.5, 139.2, 135.9, 130.1, 129.7, 129.1, 128.4, 124.0, 59.4, 23.2; IR(NaCl): ν = 3282, 3051, 1702, 1656, 1604, 1527, 1347 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{16}H_{15}N_2O_4$ $[M + H]^+$: 299.1032; found: 299.1035.



***N*-(1-(4-methoxyphenyl)-2-oxo-2-phenylethyl)acetamide (3c)**

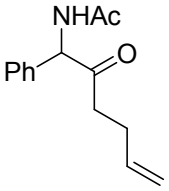
White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97-7.94 (m, 2H), 7.52-7.47 (m, 1H), 7.40-7.35 (m, 2 H), 7.32-7.27 (m, 2H), 7.07 (d, *J* = 7.0 Hz, 1H), 6.83-6.80 (m, 2H), 6.54 (d, *J* = 7.4

Hz, 1H), 3.72 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.1, 169.4, 159.6, 134.5, 133.8, 129.6, 129.5, 129.2, 128.8, 114.7, 58.0, 55.3, 23.4; IR(NaCl): ν = 3288, 3086, 2958, 1732, 1691, 1610, 1513, 1372, 1255 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{17}H_{18}NO_3$: 284.1287; found: 284.1289.



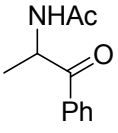
***N*-(2-oxo-1-phenylpropyl)acetamide (3d)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.28 (m, 5H), 6.94 (br s, 1H), 5.57 (d, *J* = 6.6 Hz, 1H), 2.11 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 203.8, 169.5, 136.6, 129.4, 128.7, 128.1, 63.6, 27.3, 23.2; IR(NaCl): ν = 3295, 3033, 1724, 1653, 1539, 1372 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{11}H_{14}NO_2$ $[M + H]^+$: 192.1025; found: 199.1022.



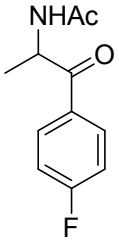
***N*-(2-oxo-1-phenylhex-5-enyl)acetamide (3e)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.28 (m, 5H), 6.98 (d, *J* = 5.6 Hz, 1H), 5,72-5.61 (m, 1H), 5.58 (d, *J* = 6.5 Hz, 1H), 4.95-4.89 (m, 2H), 2.59-2.41 (m, 2H), 2.36-2.15 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 205.4, 169.5, 136.5, 136.4, 129.3, 128.7, 128.2, 115.7, 63.1, 39.0, 27.6, 23.1; IR(NaCl): ν = 3290, 1724, 1670, 1665, 1653, 1539, 1507, 1372 cm^{-1}; HRMS (EI): m/z calcd. for $C_{14}H_{17}NO_2$: 231.1259; found: 231.1258.



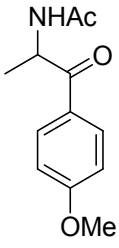
***N*-(1-oxo-1-phenylpropan-2-yl)acetamide (3f)**[10]

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.4 Hz, 2H), 7.64-7.59 (m, 1H), 7.53-7.41 (m, 2H), 6.75 (br s, 1H), 5.58 (m, 1H), 2.06 (s, 3H), 1.43 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.3, 169.6, 134.1, 134.0, 129.0, 128.9, 50.2, 23.5, 20.0.



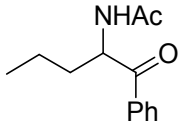
***N*-(1-(4-fluorophenyl)-1-oxopropan-2-yl)acetamide (3g)** [10]

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.06-8.02 (m, 2H), 7.21-7.15 (m, 2H), 6.71 (br s, 1H), 5.60-5.50 (m, 1H), 2.06 (s, 3H), 1.42 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.8, 169.7, 168.1, 164.7, 131.7, 131.6, 116.4, 116.1, 50.0, 23.4, 19.8.



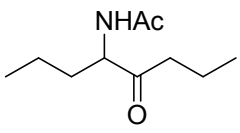
***N*-(1-(4-methoxyphenyl)-1-oxopropan-2-yl)acetamide (3h)** [10]

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.8 Hz, 2H), 6.97(d, *J* = 8.6 Hz, 2H), 6.76 (br s, 1H), 5.52 (m, 1H), 3.89 (s, 3H), 2.06 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.7, 169.6, 164.3, 131.3, 126.8, 114.2, 55.7, 49.8, 23.5, 20.3.



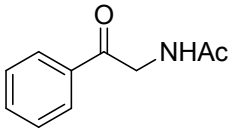
***N*-(1-oxo-1-phenylpentan-2-yl)acetamide (3i)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00-7.98 (m, 2H), 7.63-7.59 (m, 1H), 7.52-7.47 (m, 2H), 6.56 (d, *J* = 7.2 Hz, 1H), 5.68-5.61 (m, 1H), 2.07 (s, 3H), 1.95-1.85 (m, 1H), 1.64-1.52 (m, 1H), 1.44-1.18 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.5, 169.9, 134.7, 134.0, 129.1, 128.8, 53.8, 35.7, 23.5, 18.5, 14.0; IR(NaCl): ν = 3284, 3064, 2960, 2873, 1692, 1651, 1597, 1581, 1449, 1374 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{13}H_{18}NO_2$: 220.1338; found: 220.1335.



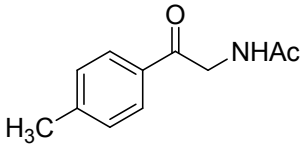
***N*-(5-oxooctan-4-yl)acetamide (3j)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.37 (d, *J* = 6.4 Hz, 1H), 4.66 (dt, J = 7.3, 4.6 Hz, 1H), 2.52-2.47 (m, 2H), 2.02 (s, 3H), 1.91-1.80 (m, 1H), 1.69-1.57 (m, 2H), 1.56-1.47 (m, 1H), 1.41-1.18 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.6, 170.0 58.0, 42.0, 33.8, 23.3, 18.5, 17.1, 14.0, 13.8; IR(NaCl): ν = 3287, 3065, 2962, 2935, 2875, 1720, 1651, 1554, 1467, 1374 cm^{-1}; HRMS (EI): m/z calcd. for $C_{10}H_{19}NO_2$: 185.1416; found: 185.1413.



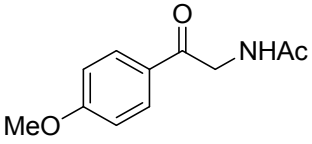
***N*-(2-oxo-2-phenylethyl)acetamide (3k)**[11]

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00-7.97 (m, 2H), 7.66-7.60 (m, 1H), 7.53-7.48 (m, 2H), 6.68 (br s, 1H), 4.78 (d, *J* = 4.3 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.4, 170.5, 134.5, 134.3, 129.1, 128.1, 46.7, 23.2.



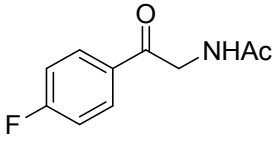
***N*-(2-oxo-2-p-tolylethyl)acetamide (3l)**

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.89-7.86 (m, 2H), 7.31-7.28 (m, 2H), 6.71 (br s, 1H), 4.74 (d, *J* = 4.3 Hz, 2H), 2.43 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.0, 170.4, 145.4, 132.0, 129.7, 128.2, 46.6, 23.2, 21.9; IR(NaCl): ν = 3076, 3043, 2924, 1690, 1650, 1606, 1548, 1373, 1243 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{11}H_{14}NO_2$: 192.1025; found: 192.1023.



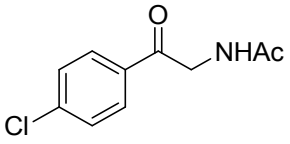
***N*-(2-(4-methoxyphenyl)-2-oxoethyl)acetamide (3m)**[12]

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98-7.93 (m, 2H), 6.99-6.94 (m, 2H), 6.72 (br s, 1H), 4.71 (d, J = 4.3 Hz, 2H), 3.88 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.7, 170.4, 164.4, 130.4, 127.5, 114.2, 55.7, 46.3, 23.2.



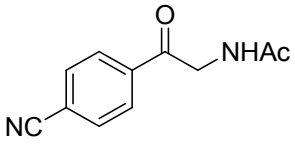
***N*-(2-(4-fluorophenyl)-2-oxoethyl)acetamide (3n)**

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.06-7.99 (m, 2H), 7.22-7.14 (m, 2H), 6.66 (br s, 1H), 4.75 (d, *J* = 4.3 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.9, 170.5, 168.2, 164.8, 131.0, 130.9, 130.8, 130.7, 116.5, 116.2, 46.6, 23.2; IR(NaCl): ν = 3308, 3110, 3055, 2987, 2940, 2306, 1682, 1650, 1600, 1510, 1266 cm^{-1}; HRMS (FAB): calcd. for $C_{10}H_{11}FNO_2$: 196.0774; found: 196.0777.



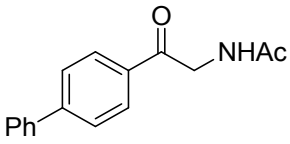
***N*-(2-(4-chlorophenyl)-2-oxoethyl)acetamide (3o)**

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94-7.91 (m, 2H), 7.49-7.47 (m, 2H), 6.65 (br s, 1H), 4.74 (d, *J* = 4.4 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.3, 170.5, 140.9, 132.8, 129.5, 77.4, 46.6, 23.2; IR(NaCl): ν = 3314, 3055, 3032, 2987, 1682, 1646, 1594, 1426 cm^{-1}; HRMS (EI): m/z calcd. for $C_{10}H_{10}ClNO_2$: 211.0400; found: 211.0403.



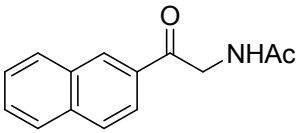
***N*-(2-(4-cyanophenyl)-2-oxoethyl)acetamide (3p)**

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 6.61 (br s, 1H), 4.80 (d, *J* = 4.5 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.4, 170.5, 137.4, 132.9, 128.5, 117.8, 117.5, 47.0, 23.2; IR(NaCl): ν = 3299, 3094, 3053, 2924, 2235, 1696, 1653, 1560, 1405, 1373, 1223 cm^{-1}; HRMS (EI): m/z calcd. for $C_{11}H_{10}N_2O_2$: 202.0742; found: 202.0741.



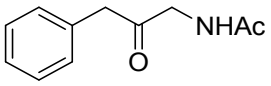
***N*-(2-(biphenyl-4-yl)-2-oxoethyl)acetamide (3q)**

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.05-8.03 (m, 2H), 7.72-7.69 (m, 2H), 7.63-7.61 (m, 2H), 7.50-7.38 (m, 3H), 6.72 (br s, 1H), 4.79 (d, *J* = 4.3 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.9, 170.5, 146.9, 139.6, 133.1, 129.2, 128.7, 127.6, 127.4, 46.7, 23.2; IR(NaCl): ν = 3240, 3084, 2980, 2931, 1692, 1647, 1650, 1553, 1495, 1220 cm^{-1}; HRMS (EI): m/z calcd. for $C1_6H_{15}NO_2$: 253.1103; found: 253.1100.



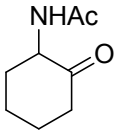
_N_-(2-(naphthalen-2-yl)-2-oxoethyl)acetamide (3r)[13]

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.50 (s, 1H), 8.02-7.86 (m, 4H), 7.65-7.54 (m, 2H), 6.75 (br s, 1H), 4.90 (d, J = 4.2 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.3, 170.5, 136.2, 132.5, 131.7, 130.1, 129.8, 129.2, 129.0, 128.0, 127.3, 123.3, 46.8, 23.3.



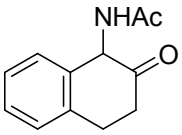
_N_-(2-oxo-3-phenylpropyl)acetamide (3s)

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.27 (m, 3H), 7.22-7.20 (m, 2H), 6.25 (br s, 1H), 4.18(d, J = 4.4 Hz, 2H), 3.74 (s, 2H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 203.3, 170.3, 133.0, 129.5, 129.2, 127.7, 50.0, 47.9, 23.1; IR(NaCl): ν = 3319, 3090, 3038, 2924, 2887, 1725, 1654, 1549, 1498, 1408, 1268 cm^{-1}; HRMS (EI): m/z calcd. for $C_{11}H_{13}NO_2$ 191.0946; found: 191.0945.



_N_-(2-oxocyclohexyl)acetamide (3u)

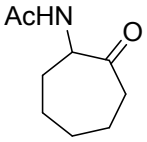
Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.48 (br s, 1H), 4.52-4.44 (m, 1H), 2.70-2.63 (m, 1H), 2.56-2.50 (m, 1H), 2.46-2.35 (m, 1H), 2.19-2.11 (m, 1H), 2.02 (s, 3H), 1.95-1.79 (m, 2H), 1.75-1.56 (m, 1H), 1.42-1.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.8, 171.6, 60.0, 43.0, 37.4, 29.9, 25.9, 25.1; IR(NaCl): ν = 3297, 3035, 2941, 2863, 1723, 1653, 1539, 1448, 1374 cm^{-1}; HRMS (FAB): m/z calcd. for $C_8H_{14}NO_2$ $[M + H]^+$: 156.1025; found: 156.1026.



_N_-(2-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (3v)[14]

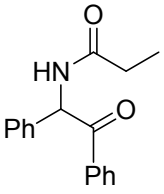
White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.31-7.21 (m, 3H), 7.17-7.13 (m, 1H), 6.50 (d, J = 5.2 Hz, 1H), 5.66 (d, J = 6.9 Hz, 1H), 3.34-3.23 (m, 1H), 3.07-2.99 (m, 1H), 2.87-2.78 (m,

1H), 2.55-2.41 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 206.6, 171.0, 136.4, 133.6, 127.9, 127.6, 127.5, 124.4, 59.7, 35.5, 27.3, 23.4.



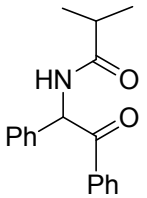
***N*-(2-oxocycloheptyl)acetamide (3w)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.70 (br s, 1H), 4.72-4.59 (m, 1H), 2.71-2.63 (m, 1H), 2.52-2.41 (m, 1H), 2.14-2.05 (m, 1H), 2.02 (s, 3H), 1.95-1.67 (m, 5H), 1.53-1.41 (m, 1H), 1.35-1.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 210.5, 169.4, 59.0, 41.6, 32.9, 29.1, 27.6, 23.4, 23.2; IR(NaCl): ν = 3281, 3067, 2929, 2855, 1712, 1651, 1544, 1444, 1377 cm^{-1}; HRMS (FAB): calcd. for $C_9H_{16}NO_2$ $[M + H]^+$: 170.1181; found: 170.1179.



***N*-(2-oxo-1,2-diphenylethyl)propionamide (5a)**

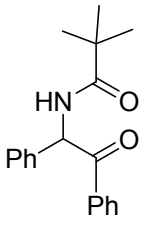
White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99-7.96 (m, 2H), 7.52-7.47 (m, 1H), 7.40-7.35 (m, 4H), 7.31-7.20 (m, 3H), 7.05 (d, J = 6.6 Hz, 1H), 6.60 (d, J = 7.3 Hz, 1H), 2.31-2.28 (m, 2H), 1.14 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.2, 173.0, 137.5, 134.5, 133.9, 129.3, 129.2, 128.8, 128.4, 128.3, 58.5, 29.6, 9.7; IR(NaCl): ν = 3283, 3062, 3030, 2969, 2914, 1688, 1669, 1629, 1958, 1580, 1529, 1496, 1293 cm^{-1}; HRMS (EI): m/z calcd. for $C_{17}H_{17}NO_2$: 267.1259; found: 267.1262.



***N*-(2-oxo-1,2-diphenylethyl)isobutyramide (5b)**

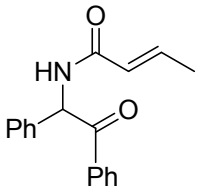
White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98-7.96 (m, 2H), 7.52-7.47 (m, 1H), 7.40-7.35 (m, 4H), 7.31-7.19 (m, 3H), 7.03 (d, J = 6.7 Hz, 1H), 6.57 (d, J = 7.3 Hz, 1H), 2.45 (m, 1H), 1.17 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.3, 176.3, 137.5, 134.6, 133.9, 129.3, 129.2, 128.8, 128.4, 128.3, 58.4, 35.5, 29.8, 19.6;

IR(NaCl): ν = 3280, 3035, 3011, 2970, 2923, 1733, 1678, 1650, 1517, 1449 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{18}H_{20}NO_2$: 282.1494; found: 282.1494.



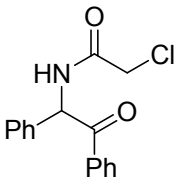
***N*-(2-oxo-1,2-diphenylethyl)pivalamide (5c)**

White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.99-7.96 (m, 2H), 7.52-7.44 (m, 1H), 7.41-7.36 (m, 4H), 7.31-7.19 (m, 4H), 6.52 (d, *J* = 7.0 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.3, 177.8, 137.5, 134.5, 133.9, 129.3, 129.2, 128.8, 128.4, 128.3, 58.6, 38.9, 27.6; IR(NaCl): ν = 3295, 3063, 3030, 2965, 2870, 1686, 1659, 1598, 1496, 1448 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{22}NO_2$: 296.1651; found: 296.1647.



***N*-(2-oxo-1,2-diphenylethyl)but-2-enamide (5d)**

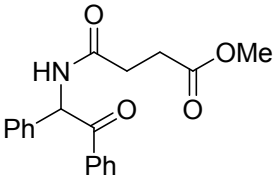
White solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.00-7.97 (m, 2H), 7.52-7.47 (m, 1H), 7.42-7.35 (m, 4H), 7.30-7.19 (m, 3H), 7.14 (d, *J* = 6.6 Hz, 1H), 6.91-6.80 (m, 1H), 6.67 (d, *J* = 7.3 Hz, 1H), 5.91 (dd, *J* = 15.2, 1.4 Hz, 1H), 1.81 (dd, *J* = 6.8, 1.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.1, 165.1, 140.8, 137.5, 134.5, 133.9, 129.3, 129.2, 128.8, 128.4, 128.3, 124.8, 58.5, 17.9; IR(NaCl): ν = 3270, 3065, 3030, 2965, 1680, 1670, 1630, 1610, 1582, 1530, 1495, 1310 cm^{-1}; HRMS (EI): m/z calcd. for $C_{18}H_{17}NO_2$: 279.1259; found: 279.1259.



2-chloro-*N*-(2-oxo-1,2-diphenylethyl)acetamide (5e)

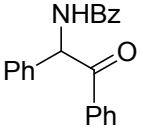
Pale yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 6.3 Hz, 1H), 7.99-7.96 (m, 2H), 7.55-7.50 (m, 1H), 7.43-7.38 (m, 4H), 7.35-7.26 (m, 3H), 6.52 (d, *J* = 7.2 Hz, 1H), 4.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.9, 165.4, 136.7, 134.2, 129.5, 129.3, 129.0,

128.9, 128.4, 58.9, 42.7; IR(NaCl): ν = 3310, 3280, 3062, 3031, 2957, 2917, 1669, 1597, 1515, 1448, 1299 cm^{-1}; HRMS (EI): m/z calcd. for $C_{16}H_{14}ClNO_2$: 287.0713; found: 278.0711.



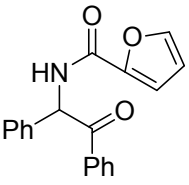
Methyl 4-oxo-4-(2-oxo-1,2-diphenylethylamino)butanoate (5f)

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97-7.95 (m, 2H), 7.52-7.47 (m, 1H), 7.40-7.35 (m, 4H), 7.31-7.20 (m, 4H), 6.57 (d, *J* = 7.2 Hz, 1H), 3.63 (s, 3H), 2.67-2.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.8, 173.3, 170.7, 137.2, 134.4, 133.9, 129.3, 129.2, 128.8, 128.5, 128.3, 58.7, 51.9, 30.9, 29.3; IR(NaCl): ν = 3314, 3063, 3030, 2952, 1737, 1690, 1669, 1597, 1580, 1520, 1448, 1226 cm^{-1}; HRMS (EI): m/z calcd. for $C_{19}H_{19}NO_4$: 325.1314; found: 325.1315.



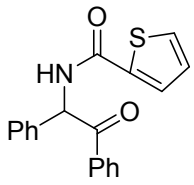
***N*-(2-oxo-1,2-diphenylethyl)benzamide (5g)**[15]

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.03-8.00 (m, 2H), 7.86-7.83 (m, 2H), 7.78 (d, *J* = 6.9 Hz, 1H), 7.53-7.45 (m, 4H), 7.43-7.37 (m, 4H), 7.33-7.21 (m, 3H), 6.76 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.0, 166.5, 137.4, 134.4, 134.0, 131.9, 129.4, 129.3, 128.9, 128.7, 128.6, 128.5, 127.3, 59.1.



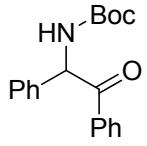
***N*-(2-oxo-1,2-diphenylethyl)furan-2-carboxamide (5h)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.02-7.99 (m, 2H), 7.88 (d, *J* = 7.2 Hz, 1), 7.52-7.36 (m, 6H), 7.33-7.20 (m, 3H), 7.10 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.72 (d, *J* = 7.4 Hz, 1H), 6.44 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.4, 157.5, 147.7, 144.3, 137.2, 134.3, 134.0, 129.4, 129.3, 128.8, 128.6, 128.4, 114.8, 112.2, 58.3; IR(NaCl): ν = 3404, 3130, 3062, 3031, 1689, 1662, 1592, 1508, 1469, 1255 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{16}NO_3$: 306.1130; found: 306.1132.



***N*-(2-oxo-1,2-diphenylethyl)thiophene-2-carboxamide (5i)**

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.01-7.98 (m, 2H), 7.70 (d, *J* = 6.7 Hz, 1H), 7.59 (d, *J* = 3.1 Hz, 1H), 7.51-7.35 (m, 6H), 7.30-7.19 (m, 3H), 7.03-7.00 (m, 1H), 6.73 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.7, 161.1, 138.6, 137.2, 134.2, 134.0, 130.5, 129.3, 129.2, 128.9, 128.6, 128.5, 128.4, 127.8, 58.9; IR(NaCl): ν = 3395, 3088, 3062, 2994, 1689, 1634, 1597, 1531, 1494, 1448, 1359 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{19}H_{16}NO_2S$ $[M + H]^+$: 322.0902; found: 322.0902.



tert-butyl 2-oxo-1,2-diphenylethylcarbamate (5j)[16]

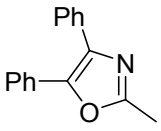
White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97-7.94 (m, 2H), 7.51-7.47 (m, 1H), 7.40-7.35 (m, 4H), 7.32-7.25 (m, 3H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.04 (d, *J* = 7.0 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.3, 155.2, 137.7, 134.7, 133.8, 129.3, 129.2, 128.8, 128.4, 128.3, 80.1, 59.9, 28.5.

5. One-pot transformation to oxazoles and a thiazole

5-a. One-pot transformation to oxazoles

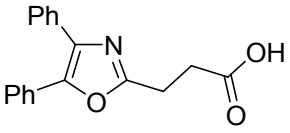
The [bmim]Cl (1.0 mL) was added to a flame-dried J-young flask then stirred at 100 °C for 1 h. The ruthenium catalyst **1** (1.0 mol%), the substrate (0.25 mmol) and triethylamine (2.0 mol%) was added under stream of argon flow and stirred at 70 °C for 12 h. Then 2 mL of sulfuric acid was added and stirred at 70 °C for 3 h. After completion of the reaction, the reaction mixture was cool down to 0 °C then H_2O (10 mL) is added dropwise. The reaction mixture was extracted with dichloromethane (3 x 10 mL), wash with H_2O (20 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulfate, and concentrated under

reduced pressure. The crude residue was purified by column chromatography to afford the corresponding oxazole.



2-methyl-4,5-diphenyloxazole (6a)[17]

Yield: 94%; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.65-7.62 (m, 2H), 7.59-7.56 (m, 2H), 7.37-7.28 (m, 6H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.3, 145.4, 135.3, 132.7, 129.2, 128.8, 128.7, 128.5, 128.1, 128.0, 126.5, 14.1.

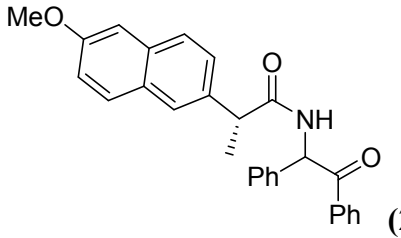


3-(4,5-diphenyloxazol-2-yl)propanoic acid (oxazprozin) (6b)[18]

Yield: 89%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 11.48 (s, 1H), 7.63-7.54 (m, 4H), 7.38-7.28 (m, 6H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 177.0, 162.1, 145.8, 135.1, 132.2, 128.9, 128.8, 128.77, 128.4, 128.2, 126.7, 31.3, 23.4.

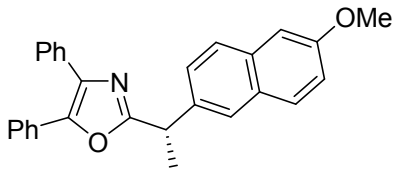
5-b. One-pot transformation to a chiral oxazole

The [bmim]Cl (0.5 mL) was added to a flame-dried J-young flask then stirred at 100 ^{o}C for 1 h. The ruthenium catalyst **1** (1.0 mol%), the substrate (0.13 mmol) and triethylamine (2.0 mol%) was added under stream of argon flow and stirred at 70 ^{o}C for 12 h. The reaction mixture was cooled down to 0 ^{o}C then $SOCl_2$ in dichloromethane (1.0 M; 1.2 equiv, 0.16 mmol) was added dropwise and stirred for 24 h at 0 ^{o}C. After completion of the reaction, H_2O (5 mL) is slowly added, extracted with dichloromethane (3 x 5 mL), wash with H_2O (10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the corresponding oxazole. Enantiomeric exccess was determined by HPLC equipped with a chiral colmun (whelk-O1, *n*-hexane:*i*-PrOH=7:3)



(2R)-2-(6-methoxynaphthalen-2-yl)-N-(2-oxo-1,2-diphenylethyl)propanamide2-oxo-1,2-diphenylethyl)acetamide (5k)

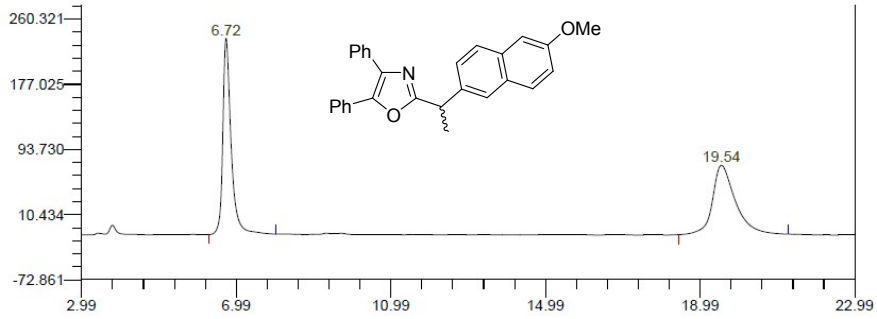
White solid; Yield: 82 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94-7.87 (m, 4H), 7.73-7.06 (m, 29 H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.54 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.0 Hz, 1H), 3.88 (s, 6H), 3.83-3.70 (m, 2H), 1.57 (d, *J* = 4.5 Hz, 3H), 1.54 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.85, 195.64, 173.67, 173.52, 157.80, 157.76, 137.35, 137.01, 136.47, 136.30, 134.49, 134.34, 133.92, 133.88, 133.84, 133.78, 129.47, 129.44, 129.29, 129.18, 129.16, 129.1, 128.81, 128.77, 128.43, 128.37, 128.23, 127.64, 127.52, 126.41, 126.39, 126.37, 126.14, 119.17, 119.10, 105.80, 105.74, 58.80, 55.43, 47.08, 46.81, 18.79; IR(NaCl): ν = 3270, 3091, 3063, 3030, 2965, 2870, 1710, 1686, 1659, 1598, 1581, 1496, 1448, 1398, 1366 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{28}H_{26}NO_3$ $[M + H]^+$: 424.1907; found: 424.1904.



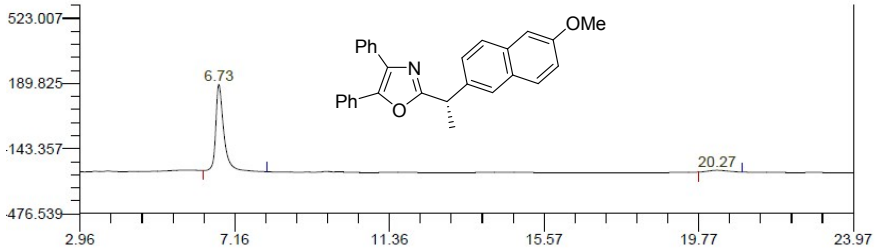
(S)-2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,5-diphenyloxazole (6c)

Yield: 70%; ee: 91%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82-7.73 (m, 5H), 7.61-7.56 (m, 3H), 7.43-7.34 (m, 6H), 7.22-7.16 (m, 2H), 4.55 (q, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 1.93 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.5, 157.8, 145.5, 137.2, 135.3, 133.8, 132.8, 129.5, 129.2, 129.1, 128.7, 128.5, 128.2, 128.17, 127.4, 126.6, 126.4, 125.9, 119.1, 105.8, 55.5, 39.9, 20.3; IR(NaCl): ν = 3058, 2977, 2934, 2852, 2106, 1955, 1904, 1737, 1678, 1634, 1607, 1566, 1506, 1485, 1444, 1393 cm^{-1}; HRMS (EI): m/z calcd. for $C_{28}H_{23}NO_2$: 405.1729; found: 405.1730.

- HPLC data



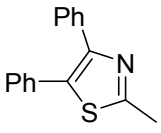
PK No.	RT	Peak Width	Area	Height	Area %	Height %	Code
1	6.724	0.208	75122507	250716	50.82219	73.91784	BB
2	19.541	0.578	72691889	88466	49.17781	26.08216	BB
Total		0.4(+/-)0.052	147814396	339182	100.00000	100.00000	



PK No.	RT	Peak Width	Area	Height	Area %	Height %	Code
1	6.728	0.209	133379348	441735	95.49186	97.99870	BB
2	20.269	0.563	6296801	9021	4.50814	2.00130	BB
Total		0.4(+/-)0.050	139676149	450756	100.00000	100.00000	

5-c. One-pot transformation to a thiazole

The [bmim]Cl (1.0 mL) was added to a flame-dried J-young flask then stirred at 100 ^{o}C for 1 h. The ruthenium catalyst **1** (1.0 mol%), the substrate (0.25 mmol) and triethylamine (2.0 mol%) was added under stream of argon flow and stirred at 70 ^{o}C for 12 h. Then Lawsson's reagent (0.5 mmol, 2.0 equiv) was added and stirred at 70 ^{o}C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature then extracted with dichloromethane (3 x 5 mL), wash with H_2O (10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the corresponding thiazole.



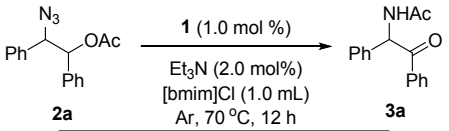
2-methyl-4,5-diphenylthiazole (7)[19]

Yield: 87%; Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51-7.48 (m, 2H), 7.31-7.24 (m, 8H), 2.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.9, 149.6, 135.1, 132.5, 132.3, 129.7, 129.1, 128.8, 128.4, 128.1, 127.8, 19.4.

6. The recycling of [bmimb]Cl

The [bmim]Cl (1.0 mL) was added to a flame-dried J-young flask then stirred at 100 °C for 1 h. The ruthenium catalyst **1** (1.0 mol%), **3a** (0.25 mmol), and triethylamine (2.0 mol%) were added under stream of argon flow and stirred at 70 °C for 12 h. After completion of the reaction, the reaction mixture was cooled down to room temperature then extracted with dichloromethane (3 x 5 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The aqueous layer was dried at 120 °C for 5 h to evaporate H_2O in an oven then reused (Table 1).

Table 2. Recycling of [bmim]Cl.



Run	Conversion[a]	Yield[a]
1	>99	96
2	>99	95
3	93	92
4	93	92
5	92	90
6	89	89

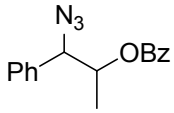
[a] Estimated by ^{1}H NMR using an internal standard.

7. Mechanistic investigation

7-a. Crossover experiment

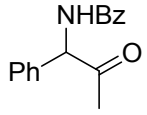
The [bmim]Cl (1.0 mL) was added to a flame-dried J-young flask then stirred at 100 °C for 1 h. The ruthenium catalyst **1** (1.0 mol%), **2a** (0.25 mmol), **8** (0.25 mmol), and triethylamine (2.0 mol%) were added under stream of argon flow and stirred at 70 °C for 12 h. Then Lawsson's reagent (2.0 equiv) was added and stirred at 70 °C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature then extracted with

dichloromethane (3x5 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The yield of **3a** and **9** were determined by ^{1}H NMR using dibromomethane as an internal standard.



1-azido-1-phenylpropan-2-yl benzoate (8)

Yield: 83%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.04-8.02 (m, 2H), 7.60-7.54 (m, 1H), 7.47-7.30 (m, 7H), 5.45-5.37 (m, 1H), 4.92 (d, *J* = 4.3 Hz, 1H), 1.31 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.0, 136.2, 133.4, 130.2, 129.9, 128.9, 128.6, 127.5, 74.0, 68.8, 14.8; IR(NaCl): ν = 3090, 3064, 3033, 2989, 2939, 2105, 1717, 1602, 1585, 1495, 1451, 1383, 1353 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{16}H_{16}N_3O_2$ $[M + H]^+$: 282.1242; found: 282.1243.



***N*-(2-oxo-1-phenylpropyl)benzamide (9)**

Yield: 91%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83-7.80 (m, 2H), 7.58 (d, *J* = 5.5 Hz, 1H), 7.53-7.30 (m, 8H), 5.73 (d, *J* = 6.1 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 203.8, 166.5, 136.7, 133.9, 132.0, 129.5, 128.9, 128.8, 128.2, 127.3, 64.1, 27.4; IR(NaCl): ν = 3320, 3062, 3031, 2918, 1720, 1649, 1602, 1580, 1514, 1483, 1455, 1358 cm^{-1}; HRMS (EI): m/z calcd. for $C_{16}H_{15}NO_2$: 253.1103; found: 253.1102.

7-b. Deportection of MOM-protected enol amide

The deprotection of MOM-protected enol amide was carried out according to a literature procedure.[20] To a solution of MOM-protected enol amide[21] (0.125 mmol) in DMF (1.0 mL) were added $ZnBr_2$ (2.0 equiv) and n-PrSH (2.0 equiv), and the mixture was stirred at 70 ^{o}C for 12 h, and dilluted with diethyl ether (5.0 mL). Saturated $NaHCO_3$ aqueous solution was added slowly at 0 ^{o}C, and the mixture was filtered through a filter paper. The filtrate was extracted with diethyl ether (3 x 5 mL). The organic layer was washed with H_2O (15 mL) and brine (15 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The yield of **3a** was determined by ^{1}H NMR using dibromomethane as an internal standard.

8. References

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