Supporting Information
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Supporting Information

Microwave Assisted Synthesis of Regiospecific Pseudohalohydrin esters

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Experimental Section

General

All reagents were available commercially. Melting points were determined on a capillary point apparatus equipped with a digital thermometer and are uncorrected. The NMR spectra were recorded in CDCl$_3$ with TMS for $^1$H (300 MHz) and $^{13}$C (75 MHz) as an internal reference. Silica gel was utilized for column chromatography.

General Procedure for the Preparation of N-Acylbenzotriazoles 1

![Chemical Reaction Diagram]

Thionyl chloride (0.6 mL, 8.00 mmol, 1.2 equiv) was added to a solution of 1H-benzotriazole (3.17 g, 26.67 mmol, 4 equiv) in methylene chloride to give a clear yellow solution that was stirred for 15 min at room temperature. The carboxylic acid (6.67 mmol, 1 equiv) was then added to give a suspension which was stirred for 2.5 h at room temperature. The suspension was filtered, the filtrate evaporated, the residue dissolved in EtOAc and the solution washed with a saturated solution of sodium carbonate. The organic portion was dried over anhydrous MgSO$_4$, filtered, and dried to give the corresponding N-acylbenzotriazoles 1.

(1H-Benzotriazol-1-yl)(4-ethylphenyl)methanone (1a): white microcrystals (91%); mp 112.0 - 113.0 °C; $^1$H NMR (CDCl$_3$): δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.88-7.64 (m, 3H), 7.26 (t, $J = 7.1$ Hz, 1H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.01-6.98
(m, 2H), 2.36 (q, \( J = 7.3 \) Hz, 2H), 0.90 (t, \( J = 7.7 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 166.3, 150.7, 145.5, 132.2, 131.9, 130.1, 128.6, 127.9, 126.0, 119.9, 114.6, 28.9, 15.0; Anal. Calcd for C\(_{15}\)H\(_{13}\)N\(_3\)O: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.96; H, 5.56; N, 16.97.

1-(1\(H\)-Benzotriazol-1-yl)-3-phenylpropan-1-one (1b): white microcrystals (90%); mp 71.0 - 72.0 °C (lit. mp 62.0-64.0 °C)\(^1\); \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.26-8.22 (m, 1H), 8.07-8.04 (m, 1H), 7.59 (tt, \( J = 8.1, 1.5 \) Hz, 1H), 7.45 (tt, \( J = 7.2, 1.5 \) Hz, 1H), 7.28-7.24 (m, 4H), 7.21-7.15 (m, 1H), 3.72 (td, \( J = 7.8, 1.1 \) Hz, 2H), 3.19 (t, \( J = 7.7 \) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 171.6, 146.1, 139.8, 131.0, 130.4, 128.6, 128.4, 126.5, 126.1, 120.1, 114.4, 37.1, 30.1; Anal. Calcd for C\(_{15}\)H\(_{13}\)N\(_3\)O: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.91; H, 5.59; N, 16.99.

(1\(H\)-Benzotriazol-1-yl)(naphthalen-2-yl)methanone (1c): white microcrystals (76%); mp 140.0-142.0 °C (lit. mp 136.0-137.0 °C)\(^2\); \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.50-8.47 (m, 1H), 8.19-8.09 (m, 3H), 7.98-7.91 (m, 2H), 7.77-7.71 (m, 1H), 7.63-7.53 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 167.8, 146.3, 133.7, 133.2, 132.2, 131.2, 130.7, 130.4, 129.5, 128.9, 128.1, 126.9, 126.7, 124.9, 124.5, 120.5, 114.9.

(1\(H\)-Benzo[d][1,2,3]triazol-1-yl)(4-nitrophenyl)methanone (1d): white microcrystals (75%); mp 199.0 - 200.0 °C (lit. mp 194.0 - 196.0 °C)\(^3\); \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.42-8.34 (m, 5H), 8.18 (d, \( J = 8.1 \) Hz, 1H), 7.75 (t, \( J = 7.7 \) Hz, 1H), 7.59 (t, \( J =7.7 \) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 165.2, 150.6, 146.0, 137.1, 132.8, 131.1, 131.2, 127.2, 123.7, 120.7, 114.9.

(1\(H\)-Benzotriazol-1-yl)(phenyl)methanone (1e): white microcrystals (90%); mp 119.0 - 120.0 °C (lit. mp 112.0 - 113.0 °C)\(^4\); \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.36 (d, \( J = 8.4 \) Hz, 2H), 7.64 (t, \( J =7.8 \) Hz, 1H), 7.51 (t, \( J =7.7 \) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 164.1, 150.4, 146.0, 137.1, 132.8, 131.1, 131.2, 127.2, 123.7, 120.7, 114.9.
Hz, 1H), 8.23-8.15 (m, 3H), 7.70-7.49 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 166.8, 145.9, 133.8,132.5, 131.9, 131.6, 130.5, 128.6, 126.5, 120.3, 114.9.

2-((3r,5r,7r)-Adamantan-1-yl)-1-(1\(H\)-benzo[d][1,2,3]triazol-1-yl)ethanone (1f): white microcrystals (74%); mp 92.0-93.0 °C (lit. mp 84.0-85.0 °C); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.33-8.29 (m, 1H), 8.11-8.07 (m, 1H), 7.65-7.59 (m, 1H), 7.51-7.45 (m, 1H), 3.19 (s, 2H), 1.96 (br s, 3H), 1.73-1.74 (m, 12H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 171.1, 146.5, 131.2, 130.4, 126.2, 120.3, 114.9, 48.4, 42.7, 36.8, 34.7, 28.8.

\(\text{(S)}\)-Benzyl (1-(1\(H\)-benzo[d][1,2,3]triazol-1-yl)-1-oxo-3-phenylpropan-2-yl)carbamate (1g): white microcrystals (90%); mp 150.0 - 152.0 °C (lit. mp 152.0 - 153.0 °C); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.23 (d, \(J = 7.8\) Hz, 1H), 8.15 (d, \(J = 7.8\) Hz, 1H), 7.68 (t, \(J = 7.4\) Hz, 1H), 7.54 (t, \(J = 7.5\) Hz, 1H), 7.32-7.23 (m, 7H), 7.14 (br s, 3H), 6.09 (d, \(J = 4.2\) Hz, 1H), 5.57 (d, \(J = 6.6\) Hz, 1H), 5.08 (s, 2H), 3.48 (d, \(J = 9.6\) Hz, 1H), 3.24 (d, \(J = 7.8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 170.8, 155.7, 146.0, 135.9, 134.9, 131.0, 130.8, 129.2, 128.7, 128.5, 128.1, 127.4, 126.5, 120.4, 114.3, 67.2, 55.6, 38.8.
General Procedure for the Preparation of β-(benzotriazol-1-yl)ethyl esters 4

To a mixture of \(N\)-acylbenezotriazoles 1 (0.20 mmol) and \(\text{Pd(PPh}_3\text{)}_4\) (23.11 mg, 10 mol\%) in a microwave tube was added epoxide 3 (1.5 equiv). The mixture was stirred at 130 °C and 50 W for 30 min. \((N\text{-aroylbenezotriazoles}) - 60\) min. \((N\text{-alkylbenezotriazoles})\). The residue was dissolved in MeOH and purified by silica gel column chromatography to obtain the corresponding hydrid esters 4. Table 1 summarizes optimization of the reaction condition.
2-(1H-Benzotriazol-1-yl)-1-phenylethyl 4-ethylbenzoate (4a):

purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 7:3) to obtain a yellow oil, (87%); \(^1\)H NMR (CDCl\(_3\)):

\[\delta 7.83 (d, J = 8.1 \text{ Hz}, 1H), 7.69 (d, J = 8.1 \text{ Hz}, 1H), 7.27-7.14 (m, 10H), 7.06-7.01 (m, 1H), 6.29-6.25 (m, 1H), 5.00-4.86 (m, 2H), 2.48 (q, J = 7.4 \text{ Hz}, 2H), 1.03 (t, J = 7.5 \text{ Hz}, 3H); \]
\(^{13}\)C NMR (CDCl\(_3\)):

\[\delta 165.3, 150.3, 136.7, 133.4, 129.9, 128.9, 128.0, 127.4, 126.3, 125.7, 123.9, 120.9, 109.3, 74.3, 52.8, 29.0, 15.2; \]
HRMS m/z for C\(_{23}\)H\(_{22}\)N\(_3\)O\(_2\) [M+H]\(^+\) calcd. 372.1707, found 372.1703.

2-(1H-Benzotriazol-1-yl)-1,2-diphenylethyl 4-ethylbenzoate (4b): purified by gradient silica gel column chromatography (hexanes to hexanes:CH\(_2\)Cl\(_2\), 3:2, then hexanes:CH\(_2\)Cl\(_2\), 1:1) to obtain beige microcrystals, (62%), mp 109.0-110.0 °C; \(^1\)H NMR (CDCl\(_3\)):

\[\delta 8.09 (dd, J = 8.3, 1.4 \text{ Hz}, 1H), 7.68-7.60 (m, 2H), 7.54-7.47 (m, 1H), 7.45-7.30 (m, 6H), 7.27-7.20 (m, 6H), 7.14-7.11 (m, 2H), 6.34 (dd, J = 9.2, 1.4 \text{ Hz}, 1H), 2.82-2.73 (m, 1H), 2.65 (q, J = 7.5 \text{ Hz}, 2H), 1.35-1.28 (m, 2H), 1.22 (td, J = 7.8, 2.1 \text{ Hz}, 3H); \]
\(^{13}\)C NMR (CDCl\(_3\)):

\[\delta 165.0, 149.9, 136.8, 134.6, 133.3, 130.2, 129.6, 128.8, 128.7, 128.6, 128.4, 128.2, 128.0, 127.7, 127.3, 127.2, 126.8, 125.9, 123.9, 120.1, 109.6, 76.8, 67.4, 28.8, 15.1; \]
HRMS m/z for C\(_{29}\)H\(_{26}\)N\(_3\)O\(_2\) [M+H]\(^+\) calcd.448.2020, found 448.2022.

1-(1H-Benzo[d][1,2,3]triazol-1-yl)hexan-2-yl 3-phenylpropanoate (4c): purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 4:1) to obtain yellow oil, (72%); \(^1\)H NMR (CDCl\(_3\)):

\[\delta 8.05-8.01 (m, 1H), 7.49-7.42 (m, 2H), 7.36-7.31 (m, 1H), 7.29-7.07 (m, 5H), 5.28-5.21 (m, 1H), 4.74 (dd, J = 14.6, 4.8 \text{ Hz}, 1H),\]
4.69 (dd, $J = 14.5$, 6.1 Hz, 1H), 2.97-2.40 (m, 4H), 1.59-1.52 (m, 2H), 1.30-1.19 (m, 4H), 0.83 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 172.4, 145.9, 140.27, 133.7, 128.6, 128.4, 127.7, 126.5, 124.2, 120.2, 109.7, 72.5, 50.9, 35.9, 31.5, 30.9, 27.3, 22.6, 14.1.

2-(1H-Benzod[1,2,3]triazol-1-yl)-1-phenylethyl 1-naphthoate (4d):
purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 9.3:0.7) to obtain white solid, (62%); mp 62.0-63.0°C $^1$H NMR (CDCl$_3$): $\delta$ 8.60-8.56 (m, 1H), 8.09-7.97 (m, 3H), 7.85-7.79 (m, 1H), 7.50-7.26 (m, 11H), 6.58 (dd, $J = 7.5$, 4.7 Hz, 1H), 5.19 (dd, $J = 14.6$, 7.5 Hz, 1H), 5.11 (dd, $J = 14.6$, 4.7 Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$ 166.1, 146.0, 136.9, 134.0, 133.9, 133.6, 131.4, 130.6, 129.2, 128.7, 128.1, 127.7, 126.6, 126.5, 125.7, 124.6, 124.1, 120.3, 109.5, 74.7, 53.1; Anal. Calcd for C$_{25}$H$_{19}$N$_3$O$_2$: C, 76.32; H, 4.87; N, 10.68. Found: C, 75.97; H, 5.31; N, 10.45.

1-(1H-Benzod[1,2,3]triazol-1-yl)hexan-2-yl 1-naphthoate (4e):
purified by gradient silica gel column chromatography (hexanes to EtOAc:hexanes, 9.3:0.7) to obtain a yellow oil (73%); $^1$H NMR (CDCl$_3$): $\delta$ 8.64-8.59 (m, 1H), 8.02-7.89 (m, 3H), 7.79-7.75 (m, 1H), 7.51-7.17 (m, 6H), 5.61-5.53 (m, 1H), 4.88 (d, $J = 5.3$ Hz, 2H), 1.78-1.70 (m, 2H), 1.51-1.22 (m, 4H), 0.81 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 166.8, 146.1, 133.9, 133.7, 131.5, 130.5, 128.7, 128.0, 127.6, 126.5, 126.4, 125.7, 124.6, 124.1, 120.2, 109.9, 72.8, 51.0, 31.7, 27.6, 22.6, 14.1; Anal. Calcd for C$_{69}$H$_{73}$N$_9$O$_8$: C, 71.67; H, 6.36; N, 10.90. Found: C, 71.53; H, 6.38; N, 10.93.
2-(1H-Benz[d][1,2,3]triazol-1-yl)-1-phenylethyl 4-nitrobenzoate (4f): purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 9:1) to obtain a yellow oil (70%); $^1$H NMR (CDCl$_3$): $\delta$ 8.31-8.11 (m, 7H), 7.52-7.34 (m, 5H), 6.44 (dd, $J = 8.4$, 3.6 Hz, 1H), 4.82 (dd, $J = 12.0$, 8.4 Hz, 1H), 4.71(dd, $J =12.2$, 3.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$ 164.5, 164.0, 151.0, 135.6, 135.2, 135.1, 131.1, 131.0, 129.5, 129.3, 126.9, 123.9, 75.1, 67.3.

2-(1H-Benzotriazol-1-yl)-1-phenylethyl benzoate (4g): purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 9:1) to obtain a yellow oil (75%); $^1$H NMR (CDCl$_3$): $\delta$ 8.02-7.93 (m, 3H), 7.55-7.27 (m, 11H), 6.46 (dd, $J = 7.5$, 4.8 Hz, 1H), 5.15 (dd, $J = 14.5$, 7.3 Hz, 1H), 5.07 (dd, $J = 14.5$, 4.8, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$ 165.4, 145.9, 136.8, 133.6, 129.9, 129.5, 129.2, 129.1, 128.6, 127.6, 126.5, 124.1, 120.2, 109.4, 74.7, 52.9; HRMS m/z for C$_{21}$H$_{18}$N$_3$O$_2$ [M+H]$^+$ calcd. 344.1394, found 344.1384.

1-(1H-Benz[d][1,2,3]triazol-1-yl)hexan-2-yl benzoate (4h): purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 9:1) to obtain a yellow oil (76%); $^1$H NMR (CDCl$_3$): $\delta$ 8.03-8.00 (m, 1H), 7.91-7.88 (m, 2H), 7.55-7.49 (m, 2H), 7.40-7.28 (m, 4H), 5.55-5.48 (m, 1H), 4.90 (d, $J = 5.2$ Hz, 2H), 1.76-1.67 (m, 2H), 1.47-1.26 (m, 4H), 0.85 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 166.1, 146.1, 133.7, 133.5, 129.9, 129.7, 128.6, 127.6, 124.1, 120.2, 109.9, 72.9, 50.9, 31.5, 27.5, 22.6, 14.0; HRMS m/z for C$_{19}$H$_{22}$N$_3$O$_2$ [M+H]$^+$ calcd. 324.1707, found 324.1719.
1-(1H-Benzo[d][1,2,3]triazol-1-yl)hexan-2-yl acetate (4i): purified by gradient silica gel column chromatography (hexanes to hexanes:EtOAc, 9.3:0.7) to obtain a yellow oil (52%); $^1$H NMR (CDCl$_3$): $\delta$ 8.00-7.97 (m, 1H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.47-7.41 (m, 1H), 7.33-7.28 (m, 1H), 5.27-5.19 (m, 1H), 4.72-4.69 (m, 2H), 2.05-1.88 (m, 3H), 1.84-1.80 (m, 2H), 1.63-1.55 (m, 8H), 1.49-1.46 (m, 2H), 1.37-1.18 (m, 8H), 0.82 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 171.3, 146.0, 133.8, 127.7, 124.1, 120.2, 109.9, 71.9, 50.9, 49.0, 42.5, 42.4, 36.9, 36.8, 32.9, 31.7, 28.8, 28.7, 27.5, 22.6, 14.1; HRMS m/z for C$_{24}$H$_{33}$N$_3$O$_2$Na [M+Na]$^+$ calcd. 418.2465, found 418.2480.

1-(1H-Benzotriazol-1-yl)hexan-2-ol (5a): purified by gradient silica gel column chromatography (hexanes to EtOAc:hexanes, 4:1) to obtain a yellow oil (70%); $^1$H NMR (CDCl$_3$): $\delta$ 7.96 (dd, $J = 8.4$, 0.9 Hz, 1H), 7.60 (dd, $J = 8.7$, 0.9 Hz, 1H), 7.50-7.45 (m, 1H), 7.36-7.30 (m, 1H), 4.71-4.64 (m, 2H), 4.56-4.49 (m, 1H), 4.25 (br s, 1H), 1.65-1.34 (m, 6H), 0.92 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (CDCl$_3$): $\delta$ 145.5, 133.8, 128.5, 127.4, 124.0, 119.7, 109.9, 71.0, 54.0, 34.3, 27.6, 22.6, 14.0; HRMS m/z for C$_{12}$H$_{17}$N$_3$ONa [M+Na]$^+$ calcd. 242.1264, found 242.1266.
References


$^1$H NMR and $^{13}$C NMR spectra for compounds \textbf{1a-g} and \textbf{4a-j}