Electronic Supplementary Information

Palladium-Catalyzed β-selective C(sp²)−H Carboxamidation of Enamides by Isocyanide Insertion: Synthesis of N-acyl Enamine Amides

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I. General Information

$^1$H NMR (400 MHz) and $^{13}$C NMR (125 MHz) were registered on 400 M and 500 M spectrometers. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H spectrum as 0.00 ppm, CDCl$_3$ resonance in the $^{13}$C spectrum as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). NMR analysis was carried out at 298 K unless noted otherwise. HRMS was obtained on an ESI-LC-MS/MS spectrometer.

II. General Procedure

![General procedure](image)

General procedure: To an oven-dried 10 mL schlenk tube charged with enamide (0.2 mmol), Pd(OAc)$_2$ (0.01 mmol, 2.24 mg), Cu(OPiv)$_2$ (0.2 mmol, 53.2 mg) and CsOPiv (0.2 mmol, 46.8 mg) was added a solution of t-BuNC (0.3 mmol, 34.0 μL) and H$_2$O (0.2 mmol, 3.6 μL) in 2.0 mL of dry DCE by syringe. The mixture was stirred at 80 °C under air. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and quenched with 2 mL of NH$_3$.H$_2$O. The crude reaction mixture was extracted with EA (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

III. Characterization Data

(Z)-3-acetamido-N-(tert-butyl)-3-phenylacrylamide(3a)
Prepared from N-(1-phenylvinyl)acetamide (32.2 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column
chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3a as a colorless oil (39 mg, 0.15 mmol, 75% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.53 (s, 1H), 7.30 (brs, 5H), 5.46 (s, 1H), 4.94 (s, 1H), 2.13 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.7, 167.8, 150.9, 136.8, 128.9, 127.9, 126.9, 104.8, 51.6, 28.9, 24.9; HRMS: calcd for C$_{15}$H$_{20}$N$_2$O$_2$(M+H$^+$) 261.1598; found 261.1599.

(Z)-3-acetamido-$N$-(tert-butyl)-3-(o-tolyl)acrylamide(3b)
Prepared from $N$-(1-(o-tolyl)vinyl)acetamide (35.0 mg, 0.2 mmol, 1.0 equiv) and $t$-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3b as a colorless oil (32 mg, 0.12 mmol, 58% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 11.89 (s, 1H), 7.24-7.20 (m, 1H), 7.16-7.09 (m, 3H), 5.27 (s, 1H), 4.67 (s, 1H), 2.25 (s, 3H), 2.08 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.3, 167.7, 151.3, 137.0, 135.5, 129.6, 128.4, 127.6, 125.5, 102.7, 51.6, 29.1, 24.8, 19.6; HRMS: calcd for C$_{16}$H$_{22}$N$_2$O$_2$(M+H$^+$) 275.1754; found 275.1754.

(Z)-3-acetamido-$N$-(tert-butyl)-3-(m-tolyl)acrylamide(3c)
Prepared from $N$-(1-(m-tolyl)vinyl)acetamide (35.0 mg, 0.2 mmol, 1.0 equiv) and $t$-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3c as a colorless oil (35 mg, 0.13 mmol, 64% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 11.49 (s, 1H), 7.22-7.19 (m, 1H), 7.15-7.11 (m, 3H), 5.33 (s, 1H), 4.95 (s, 1H), 2.34 (s, 3H), 2.14 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.7, 167.8, 151.4, 137.6, 136.8, 129.8, 127.9, 127.5, 124.2, 104.5, 51.6, 29.1, 25.0, 21.6; HRMS: calcd for C$_{16}$H$_{22}$N$_2$O$_2$(M+H$^+$) 275.1754; found 275.1757.

(Z)-3-acetamido-$N$-(tert-butyl)-3-(p-tolyl)acrylamide(3d)
Prepared from $N$-(1-(p-tolyl)vinyl)acetamide (35.0 mg, 0.2 mmol, 1.0 equiv) and $t$-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column
chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3d as a colorless oil (33 mg, 0.12 mmol, 60% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.49 (s, 1H), 7.22 (d, $J$ = 8.16 Hz, 2H), 7.13 (d, $J$ = 8.16 Hz, 2H), 5.31 (s, 1H), 4.94 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.8, 167.9, 151.3, 139.1, 133.9, 128.8, 126.9, 104.1, 51.6, 29.1, 25.0, 21.5; HRMS: calcd for C$_{20}$H$_{28}$NO$_2$ (M+H$^+$) 275.1754; found 275.1761.

(Z)-3-acetamido-$N$-(tert-butyl)-3-(4-methoxyphenyl)acrylamide(3e)
Prepared from $N$-(1-(4-methoxyphenyl)vinyl)acetamide (38.2 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3e as a light yellow oil (29 mg, 0.10 mmol, 50% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 11.50 (s, 1H), 7.27 (d, $J$ = 8.8 Hz, 2H), 6.85 (d, $J$ = 8.8 Hz, 2H), 5.35 (s, 1H), 4.93 (s, 1H), 3.80 (s, 3H), 2.14 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.9, 168.0, 160.4, 150.9, 129.0, 128.4, 113.5, 103.7, 55.4, 51.6, 29.1, 25.1; HRMS: calcd for C$_{15}$H$_{19}$BrN$_2$O$_2$ (M+H$^+$) 291.1703; found 291.1716.

(Z)-3-acetamido-$N$-(tert-butyl)-3-(3-methoxyphenyl)acrylamide(3f)
Prepared from $N$-(1-(3-methoxyphenyl)vinyl)acetamide (38.2 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3f as a colorless oil (29 mg, 0.10 mmol, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.47 (s, 1H), 7.23 (t, $J$ = 7.9 Hz, 1H), 6.92-6.84 (m, 3H), 5.36 (s, 1H), 4.97 (s, 1H), 3.79 (s, 3H), 2.13 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.7, 167.8, 159.3, 151.0, 138.3, 129.1, 119.6, 114.5, 112.8, 104.7, 55.4, 51.7, 29.0, 24.9; HRMS: calcd for C$_{16}$H$_{22}$N$_2$O$_3$ (M+H$^+$) 291.1703; found 291.1703.

(Z)-3-[(1,1’-biphenyl)-4-yl]-3-acetamido-$N$-(tert-butyl)acrylamide(3g)
Prepared from $N$-(1-[(1,1’-biphenyl)-4-yl]vinyl)acetamide (47.4 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the
product 3g as a colorless oil (44 mg, 0.13 mmol, 66% yield). 1H NMR (500 MHz, CDCl3): δ 11.55 (s, 1H), 7.59 (d, J = 7.4 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 5.40 (s, 1H), 5.02 (s, 1H), 2.17 (s, 3H), 1.41 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 168.9, 167.8, 150.8, 141.9, 140.7, 135.7, 128.9, 127.6, 127.5, 126.8, 104.7, 51.7, 29.1, 25.0; HRMS: calcd for C21H24N2O2 (M+H+) 337.1911; found 337.1921.

(Z)-3-acetamido-N-(tert-butyl)-3-(4-fluorophenyl)acrylamide (3h)
Prepared from N-(1-(4-fluorophenyl)vinyl)acetamide (35.8 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3h as a light yellow oil (30 mg, 0.11 mmol, 54% yield). 1H NMR (400 MHz, CDCl3): δ 11.55 (s, 1H), 7.31-7.27 (m, 2H), 7.02-6.98 (m, 2H), 5.34 (s, 1H), 4.91 (s, 1H), 2.14 (s, 3H), 1.40 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 168.8, 167.7, 164.2 (J = 248.4 Hz), 150.2, 132.9 (J = 3.63 Hz), 128.9 (J = 8.51 Hz), 115.1 (J = 21.9 Hz), 104.6, 51.7, 29.0, 25.0; HRMS: calcd for C15H19FN2O2 (M+H+) 279.1503; found 279.1497.

(Z)-3-acetamido-N-(tert-butyl)-3-(4-chlorophenyl)acrylamide (3i)
Prepared from N-(1-(4-chlorophenyl)vinyl)acetamide (39.2 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3i as a colorless oil (40 mg, 0.14 mmol, 67% yield). 1H NMR (500 MHz, CDCl3): δ 11.54 (s, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 5.37 (s, 1H), 4.92 (s, 1H), 2.14 (s, 3H), 1.39 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 168.8, 167.6, 150.0, 135.3, 134.9, 128.3, 128.2, 104.9, 51.8, 29.0, 24.9; HRMS: calcd for C15H19ClN2O2 (M+H+) 295.1208; found 295.1216.

(Z)-3-acetamido-3-(4-bromophenyl)-N-(tert-butyl)acrylamide (3j)
Prepared from $N$-(1-(4-bromophenyl)vinyl)acetamide (48.0 mg, 0.2 mmol, 1.0 equiv) and $t$-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product $3j$ as a light yellow oil (49 mg, 0.14 mmol, 72% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 11.54 (s, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 5.40 (s, 1H), 4.92 (s, 1H), 2.14 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.8, 167.6, 150.0, 135.8, 131.2, 128.6, 123.2, 104.9, 51.8, 29.0, 24.9; HRMS: calcd for C$_{15}$H$_{19}$BrN$_2$O$_2$ (M+H$^+$) 339.0703; found 339.0710.

$N$-$\text{HAc}$

\begin{center}
\includegraphics[width=0.2\textwidth]{structure}\n\end{center}

(Z)-3-acetamido-3-(3-bromophenyl)-$N$-(tert-butyl)acrylamide($3k$)

Prepared from $N$-(1-(3-bromophenyl)vinyl)acetamide (48.0 mg, 0.2 mmol, 1.0 equiv) and $t$-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product $3k$ as a light yellow oil (36 mg, 0.11 mmol, 53% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.50 (s, 1H), 7.46-7.44 (m, 2H), 7.25-7.22 (m, 1H), 7.20-7.15 (m, 1H), 5.39 (s, 1H), 4.94 (s, 1H), 2.15 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.7, 167.5, 139.0, 131.9, 129.8, 129.5, 125.8, 122.1, 105.3, 51.8, 29.0, 24.9; HRMS: calcd for C$_{15}$H$_{19}$BrN$_2$O$_2$ (M+H$^+$) 339.0703; found 339.0700.

$N$-$\text{HAc}$

\begin{center}
\includegraphics[width=0.2\textwidth]{structure}\n\end{center}

(Z)-3-acetamido-$N$-(tert-butyl)-3-(4-(trifluoromethyl)phenyl)acrylamide($3l$)

Prepared from $N$-(1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (45.8 mg, 0.2 mmol, 1.0 equiv) and $t$-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product $3l$ as a colorless oil (44 mg, 0.13 mmol, 67% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.59 (s, 1H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 5.40 (s, 1H), 4.95 (s, 1H), 2.15 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.8, 167.4, 149.6, 139.0, 131.9, 129.8, 129.5, 125.8, 122.1, 105.3, 51.8, 29.0, 24.9; HRMS: calcd for C$_{20}$H$_{28}$NO$_2$ (M+H$^+$) 329.1471; found 329.1480.
(Z)-methyl 4-(1-acetamido-3-(tert-butylamino)-3-oxoprop-1-en-1-yl)benzoate (3m)
Prepared from methyl 4-(1-acetamidovinyl)benzoate (43.8 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3m as a colorless oil (31 mg, 0.97 mmol, 49% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.55 (s, 1H), 7.99 (d, \(J = 8.4\) Hz, 2H), 7.37 (d, \(J = 8.4\) Hz, 2H), 5.39 (s, 1H), 4.98 (s, 1H), 3.91 (s, 3H), 2.15 (s, 3H), 1.40 (s, 9H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.7, 167.5, 166.8, 150.2, 141.5, 130.4, 129.4, 127.0, 105.5, 52.3, 51.8, 29.0, 24.8; HRMS: calcd for C\(_{17}\)H\(_{22}\)N\(_2\)O\(_4\) (M+H\(^+\)) 319.1652; found 319.1666.

(Z)-3-acetamido-\(N\)-(tert-butyl)-3-(4-nitrophenyl)acrylamide (3n)
Prepared from \(N\)-(1-(4-nitrophenyl)vinyl)acetamide (41.2 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3n as a yellow oil (34 mg, 0.11 mmol, 56% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.62 (s, 1H), 8.18 (d, \(J = 8.8\) Hz, 2H), 7.45 (d, \(J = 8.8\) Hz, 2H), 5.43 (s, 1H), 4.99 (s, 1H), 2.16 (s, 3H), 1.41 (s, 9H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.8, 167.1, 148.8, 147.9, 143.5, 127.9, 123.4, 106.2, 52.0, 29.0, 24.7; HRMS: calcd for C\(_{15}\)H\(_{19}\)N\(_3\)O\(_4\) (M+H\(^+\)) 306.1448; found 306.1449.

(Z)-3-acetamido-\(N\)-(tert-butyl)-3-(2,4-dimethylphenyl)acrylamide (3o)
Prepared from \(N\)-(1-(2,4-dimethylphenyl)vinyl)acetamide (37.8 mg, 0.2 mmol, 1.0 equiv) and t-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3o as a colorless oil (31 mg, 0.11 mmol, 53% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.87 (s, 1H), 7.00 (d, \(J = 8.2\) Hz, 1H), 6.96-6.95 (m, 2H), 5.25 (s, 1H), 4.66 (s, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.07 (s, 3H), 1.40 (s, 9H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.4, 167.7, 151.5, 138.1, 135.3, 134.2, 130.5, 127.6, 126.2, 102.7, 51.6, 29.1, 24.8, 21.3, 19.6; HRMS: calcd for C\(_{17}\)H\(_{24}\)N\(_2\)O\(_2\) (M+H\(^+\)) 289.1911; found 289.1915.
(Z)-3-acetamido-\(N\)-(tert-butyl)-3-(3,4-dimethylphenyl)acrylamide(\(3p\))
Prepared from \(N\)-(1-(3,4-dimethylphenyl)vinyl)acetamide (37.8 mg, 0.2 mmol, 1.0 equiv) and \(t\)-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product \(3p\) as a colorless oil (36 mg, 0.13 mmol, 63% yield). \(^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\):} \(\delta\) 11.46 (s, 1H), 7.09-7.05 (m, 3H), 5.33 (s, 1H), 4.95 (s, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H), 1.39 (s, 9H); \(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\):} \(\delta\) 168.8, 168.0, 151.4, 137.8, 136.2, 134.3, 129.4, 128.1, 124.6, 104.1, 51.6, 29.1, 25.0, 19.9, 19.8; HRMS: calcd for C\(_{17}\)H\(_{24}\)N\(_2\)O\(_2\) (M+H\(^{+}\)) 289.1911; found 289.1915.

\[
\begin{align*}
\text{O} & \quad \text{NH}^\prime\text{Bu} \\
\text{NHAc} & \\
\end{align*}
\]

(Z)-3-acetamido-\(N\)-(tert-butyl)-3-(naphthalen-1-yl)acrylamide(\(3q\))
Prepared from \(N\)-(1-(naphthalen-1-yl)vinyl)acetamide (42.2 mg, 0.2 mmol, 1.0 equiv) and \(t\)-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product \(3q\) as a colorless oil (49 mg, 0.16 mmol, 79% yield). \(^{1}\text{H} \text{NMR (500 MHz, CDCl}_3\):} \(\delta\) 12.09 (s, 1H), 7.96-7.92 (m, 1H), 7.84-7.79 (m, 2H), 7.46-7.42 (m, 2H), 7.40 (t, \(J = 7.0\) Hz, 1H), 7.29 (d, \(J = 7.0\) Hz, 1H), 5.36 (s, 1H), 4.84 (s, 1H), 2.04 (s, 3H), 1.40 (s, 9H); \(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\):} \(\delta\) 168.2, 167.5, 150.1, 135.3, 133.1, 131.4, 128.8, 128.4, 126.5, 126.0, 125.1, 125.0, 124.8, 104.0, 51.6, 29.0, 24.7; HRMS: calcd for C\(_{19}\)H\(_{22}\)N\(_2\)O\(_2\) (M+H\(^{+}\)) 311.1754; found 311.1761.

\[
\begin{align*}
\text{O} & \quad \text{NH}^\prime\text{Bu} \\
\text{NHAc} & \\
\end{align*}
\]

(Z)-3-acetamido-\(N\)-(tert-butyl)-3-(naphthalen-2-yl)acrylamide(\(3r\))
Prepared from \(N\)-(1-(naphthalen-2-yl)vinyl)acetamide (42.2 mg, 0.2 mmol, 1.0 equiv) and \(t\)-BuNC (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product \(3r\) as a colorless oil (34 mg, 0.11 mmol, 55% yield). \(^{1}\text{H} \text{NMR (500 MHz, CDCl}_3\):} \(\delta\)
\( \text{CDCl}_3 \): \( \delta 11.63 \ (s, 1\ H), 7.81-7.79 \ (m, 3\ H), 7.76 \ (d, J = 8.5 \ \text{Hz}, 1\ H), 7.48-7.45 \ (m, 2\ H), 7.41 \ (d, J = 8.5 \ \text{Hz}, 1\ H), 5.40 \ (s, 1\ H), 5.07 \ (s, 1\ H), 2.17 \ (s, 3\ H), 1.41 \ (s, 9\ H); ^{13}\text{C} \ NMR \ (125 \ \text{MHz}, \ \text{CDCl}_3): \delta 168.8, 167.9, 151.2, 134.7, 133.7, 133.1, 128.4, 127.8, 127.3, 126.6, 126.3, 125.8, 125.2, 104.9, 51.7, 29.1, 25.0; \) HRMS: calcd for \( \text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2 \ (\text{M+H}^+) \ 311.1754; \) found 311.1761.

(Z)-3-acetamido-\( \text{N}-(\text{tert}-\text{butyl})-3-(\text{thiophen}-2\text{-yl})\text{acrylamide(3s)} \)
Prepared from \( \text{N}-(1\text{-}(\text{thiophen}-2\text{-yl})\text{vinyl})\text{acetamide} \) (33.4 mg, 0.2 mmol, 1.0 equiv) and \( \text{t-BuNC} \) (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3s as a colorless oil (32 mg, 0.12 mmol, 60% yield). \( ^1\text{H} \ NMR \ (400 \ \text{MHz}, \ \text{CDCl}_3): \delta 11.28 \ (s, 1\ H), 7.30 \ (d, J = 4.6 \ \text{Hz}, 1\ H), 7.14 \ (d, J = 4.6 \ \text{Hz}, 1\ H), 6.97 \ (t, J = 4.6 \ \text{Hz}, 1\ H), 5.41 \ (s, 1\ H), 5.20 \ (s, 1\ H), 2.16 \ (s, 3\ H), 1.38 \ (s, 9\ H); ^{13}\text{C} \ NMR \ (125 \ \text{MHz}, \ \text{CDCl}_3): \delta 169.2, 167.4, 144.0, 138.6, 127.4, 127.1, 126.7, 105.0, 52.4, 41.9, 36.4, 29.6, 25.0; \) HRMS: calcd for \( \text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_2 \ (\text{M+H}^+) \ 267.1162; \) found 267.1168.

(Z)-3-acetamido-\( \text{N}-(\text{adamantan}-1\text{-yl})-3\text{-phenylacrylamide(3t)} \)
Prepared from \( \text{N}-(1\text{-}(\text{phenylvinyl})\text{acetamide} \) (32.2 mg, 0.2 mmol, 1.0 equiv) and \( \text{AdNC} \) (48.3 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether = 1 : 4) furnished the product 3t as a colorless oil (38 mg, 0.11 mmol, 56% yield). \( ^1\text{H} \ NMR \ (400 \ \text{MHz}, \ \text{CDCl}_3): \delta 11.49 \ (s, 1\ H), 7.32-7.30 \ (m, 5\ H), 5.20 \ (s, 1\ H), 4.95 \ (s, 1\ H), 2.13 \ (s, 3\ H), 2.11 \ (\text{brs}, 3\ H), 2.05-2.01 \ (m, 6\ H), 1.71 \ (\text{brs}, 6\ H); \) \( ^{13}\text{C} \ NMR \ (125 \ \text{MHz}, \ \text{CDCl}_3): \delta 168.7, 167.6, 151.2, 136.9, 129.0, 128.0, 127.0, 104.8, 52.4, 41.9, 36.4, 29.6, 25.0; \) HRMS: calcd for \( \text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2 \ (\text{M+H}^+) \ 339.2067; \) found 339.2078.

(Z)-\( \text{N}-(3\text{-}(\text{tert}-\text{butylamino})-3\text{-oxo-1-phenylprop-1-en-1-yl})\text{benzamide(3u)} \)
Prepared from \( \text{N}-(1\text{-}(\text{phenylvinyl})\text{benzamide} \) (44.6 mg, 0.2 mmol, 1.0 equiv) and \( \text{t-BuNC} \) (24.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure. Column
chromatography purification (EtOAc : petroleum ether = 1 : 8) furnished the product **3u** as a white solid (33.2 mg, 0.11 mmol, 52% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.57 (s, 1H), 8.02 (d, $J = 7.2$ Hz , 2H), 7.56-7.46 (m, 3H), 7.41-7.33 (m, 5H), 5.38 (s, 1H), 5.09 (s, 1H), 1.41 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.1, 165.2, 151.9, 137.2, 134.3, 132.2, 129.0, 128.8, 128.2, 128.1, 127.1, 105.4, 51.8, 29.1; HRMS: calcd for C$_{20}$H$_{22}$N$_2$O$_2$ (M+H$^+$) 323.1754; found 323.1741; mp = 160-162 °C.

![3-acetamido-N-(tert-butyl)-3-phenylpropanamide](image)

3-acetamido-N-(tert-butyl)-3-phenylpropanamide(4)

To a solution of (Z)-3-acetamido-N-(tert-butyl)-3-phenylacrylamide (**3a**, 0.2 mmol) in MeOH (2 mL) was added Pd/C (50.0mg). Then the reaction mixture was stirred at r.t. under H$_2$(g) (1 atm). The reaction was monitored by TLC until completion. The crude reaction mixture was filtered to obtain filtrate. After evaporation, the product **4** can be obtained in quantitative yield without further purification.

White solid (52.2 mg, 0.2 mmol, 100% yield). mp = 210-212 °C; $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 7.38-7.28 (m, 4H), 7.36-7.21 (m, 1H), 5.29 (t, $J = 7.5$ Hz, 1H), 2.58 (d, $J = 7.5$ Hz, 2H), 1.96 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 172.2, 171.8, 142.8, 129.5, 128.4, 127.7, 52.5, 51.9, 44.4, 28.8, 22.7; HRMS: calcd for C$_{21}$H$_{26}$N$_2$O$_2$ (M+H$^+$) 263.1754; found 263.1754.
IV. Copies of $^1$H and $^{13}$C NMR Spectra

3a
3c
3h
3j
3u
NOESY spectra of 3a