Supporting Information
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Dehydrogenative Allylic Aminations of But-3-enoic Acid Derivatives

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Table of Contents

I-General remarks 1
II-Procedures and Analytical data of starting materials 2
II-a-Synthesis of allyl-amides 1a-j: General procedure (GP1) 2
II-b-Synthesis of allyl-amide 1k 5
II-c-Synthesis of allyl-amide 1l 6
III-Procedures and Analytical data of aminated product 6
III-a-Pd(II)-catalyzed direct amination (2a-i, 2l-m, 3a, 4a-e and 5a-d): General procedure (GP2) 6
III-b-Pd(II)-catalyzed direct acyloxylation (6a-k, 6m): General procedure (GP3) 14
III-c-Pd(0)-catalyzed amination (7a): procedure (GP4) 19
III-d-Sequential Pd(II) / Pd(0) catalyzed amination (7a-d, 7g-i): General procedure (GP5) 19
IV-1H, 13C and 19F NMR Spectra 23

I-General Remarks

Unless special mention, all reactions were carried out under an argon atmosphere. Glassware was flame-dried under an argon gas flow prior to use. Reactions were run in flasks or sealed tubes with magnetic stirring. Reagents and solvents were purchased from commercial sources and used as received. DCM, THF, CH3CN and DMF were dried on a Mbraun purification system MB SPS-800. Nucleophiles were synthesized according to literature procedures: TsNHCOOMe,2 TsNHCOMe,3 tBuSONHCOOMe.4 NMR spectra (1H, 13C) were recorded on a Bruker AM 300 MHz or a Bruker AVANCE 400 MHz. NMR experiments were carried out in deuterochloroform (CDCl3) and deuterodimethylsulfoxide (DMSO-d6). Chemical shift are given in parts per million (ppm) using the CDCl3 residual signal as reference or the DMSO-d6.

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residual signal as reference. Coupling constants ($J$) are given in Hertz (Hz). IR spectra were recorded on a Bruker Tensor 27 (ATR diamond) Bruker spectrophotometer and reported as characteristic bands (cm$^{-1}$). High resolution mass spectra (HRMS) were recorded at the institute Parisien de Chimie Moléculaire (FR 2769) (electrospray source). Melting points were measured in capillary tubes on Stuart Scientific SMP3 apparatus and are uncorrected.

TLC were performed on Merck 60 F254 silica gel and revealed with either a ultra-violet lamp (254 nm) or a specific color reagent (potassium permanganate, $p$-anisaldehyde, etc.). A silica gel Merck Geduran® SI 60 (40-63 mm) was used for flash column chromatography. Preparative thin layer chromatography was realized with PLC silica gel 60 F254 (1 mm, 20x20 cm.).

**II-Procedures and Analytical data**

**II-a-Synthesis of allyl-amides 1a-j: General procedure (GP1)**

To a stirred solution of corresponding amine (1.0 or 2.0 equiv) in CH$_2$Cl$_2$ (0.2 M) were added at 0 °C DCC (1.3 equiv), DMAP (0.13 equiv) and 3-butenolic acid (1.3 equiv). The reaction mixture was stirred for 10 minutes at 0 °C, then for 24 hours at room temperature. The precipitate was filtered off and washed with CH$_2$Cl$_2$ (25 mL). The organic layer was hydrolyzed with saturated aqueous NaHCO$_3$, extracted and dried over MgSO$_4$ and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding allyl-amide 1.

**N-Benzyl-3-butenamide (1a)**

Following **GP1** with benzyamine (1 equiv, 1.02 mL, 9.3 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 1a in quantitative yield (1.9 g, 10.8 mmol). White solid. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.40-7.29 (m, 5H), 6.07-5.91 (m, 2H), 5.29-5.23 (m, 2H), 4.48 (d, 2H, $J = 5.7$ Hz), 3.09 (td, 2H, $J = 1.3$, 7.2 Hz). These spectroscopic data are in good agreement with those reported in the literature.$^5$

**N-(4-methylbenzyl)-3-butenamide (1b)**

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Following GP1 with 4-methylbenzylamine (1 equiv, 500 mg, 4.1 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 1b in 76% yield (588 mg, 3.11 mmol). White solid, mp: 100-102 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.10-7.05 (m, 4H), 5.86 (ddt, 1H, $J = 16.7$, 10.5, 7.2 Hz), 5.77 (br s, 1H), 5.17-5.11 (m, 2H), 4.32 (d, 2H, $J = 5.6$ Hz), 2.97 (dt, 2H, $J = 7.1$, 1.3 Hz), 2.26 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 170.2, 137.3, 135.1, 131.3, 129.4, 127.1, 119.9, 43.4, 41.6, 21.1. IR (cm$^{-1}$) γ: 3291, 1626, 1532, 1412. HRMS (ESI) m/z calcd for C$_{12}$H$_{15}$NNaO $[M+Na]^+$: 212.1046, found 212.1046.

$N$-(4-methoxybenzyl)-3-butenamide (1c)

Following GP1 with 4-methoxybenzylamine (1 equiv, 0.47 mL, 3.64 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 1c in 96% yield (715 mg, 3.5 mmol). White solid, mp: 88-90 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.25-7.20 (m, 2H), 6.91-6.87 (m, 2H), 6.01-5.90 (m, 1H), 5.81 (br s, 1H), 5.26-5.21 (m, 2H), 4.40 (d, 2H, $J = 5.6$ Hz), 3.82 (s, 3H), 3.06 (dt, 2H, $J = 7.2$, 1.3 Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 170.2, 159.1, 131.3, 130.2, 129.1, 119.9, 114.1, 55.3, 43.2, 41.6. IR (cm$^{-1}$) γ: 3285, 1636, 1548, 1511, 1300, 1173. HRMS (ESI) m/z calcd for C$_{12}$H$_{15}$NNaO$_2$ [M+Na]$^+$: 228.0995, found 228.0992.

$N$-(3-methoxybenzyl)-3-butenamide (1d)

Following GP1 with 3-methoxybenzylamine (1 equiv, 0.47 mL, 3.6 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 1d in 82% yield (611 mg, 2.97 mmol). Orange oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.28-7.23 (m, 1H), 6.87-6.82 (m, 3H), 6.01 (m, 1H), 5.99-5.91 (m, 1H), 5.26-5.21 (m, 2H), 4.42 (d, 2H, $J = 5.7$ Hz), 3.81 (s, 3H), 3.06 (dt, 2H, $J = 7.1$, 1.3 Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 170.4, 159.8, 139.7, 131.3, 129.7, 119.9, 119.8, 113.3, 112.9, 55.2, 43.6, 41.6. IR (cm$^{-1}$) γ: 3180, 1575, 1541, 1320. HRMS (ESI) m/z calcd for C$_{12}$H$_{15}$LiNO$_2$ [M+Li]$^+$: 212.1258, found 212.1264.

$N$-(4-nitrobenzyl)-3-butenamide (1e)
Following GP1 with 4-nitrobenzylamine hydrochloride (1 equiv, 300 mg, 1.6 mmol) and DMAP (1.2 equiv, 233 mg, 1.9 mmol). The crude product was purified by flash chromatography on silica gel (eluuent: AcOEt/CycloHexane 1:1) to afford 1e in 60% yield (200 mg, 0.91 mmol). White solid, mp: 83-84 °C. 1H NMR (CDCl₃, 400 MHz): δ 8.23-8.19 (m, 2H), 7.47-7.44 (m, 2H), 6.05 (br s, 1H), 5.98 (tdd, 1H, J = 7.2, 10.2, 17.3 Hz), 5.32-5.27 (m, 2H), 4.57 (d, 2H, J = 7.2, 12.2 Hz), 5.32-5.27 (m, 2H), 4.52 (d, 2H, J = 6.1 Hz), 3.13 (dt, 2H, J = 7.2, 1.2 Hz).

13C NMR (CDCl₃, 100 MHz): δ 170.6, 145.7, 145.1, 130.9, 128.2, 123.9, 120.5, 42.8, 41.5. IR (cm⁻¹): 3229, 3055, 2926, 1638, 1601, 1545, 1345. HRMS (ESI) m/z calcd for C₁₁H₁₂N₂NaO₃ [M+Na⁺]: 243.0740, found 243.0743.

N-(4-(trifluoromethyl)benzyl)but-3-enamide (1f)

Following GP1 with 4-(trifluoromethyl)benzylamine (1 equiv, 500 mg, 5.81 mmol). The crude product was purified by flash chromatography on silica gel (eluuent: AcOEt/CycloHexane 1:1) to afford 1f in 70% yield (990 mg, 4.07 mmol). White solid, mp: 118-120 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.60 (d, 2H, J = 7.9 Hz), 7.39 (d, 2H, J = 8.0 Hz), 6.09 (br s, 1H), 5.20-5.23 (m, 2H), 4.50 (d, 2H, J = 6.0 Hz), 3.69 (dt, 1H, J = 7.1, 1.3 Hz). 13C NMR (CDCl₃, 100 MHz): δ 170.6, 142.3, 129.8 (J = 33.3 Hz), 131.1, 127.8, 125.7, 124.2 (J = 270 Hz), 120.2, 43.0, 41.5. 31F NMR (CDCl₃): δ -62.5. IR (cm⁻¹): 3476, 1647, 1545, 1328, 1029. HRMS (ESI) m/z calcd for C₁₂H₁₂F₃NNaO [M+Na⁺]: 266.0763, found 266.0761.

N-(2-furanylmethyl)-3-butenamide (1g)

Following GP1 with furfurylamine (2 equiv, 1.03 mL, 11.6 mmol). The crude product was purified by flash chromatography on silica gel (eluuent: AcOEt/CycloHexane 1:1) to afford 1g in 52% yield (490 mg, 2.97 mmol). White solid. 1H NMR (CDCl₃, 400 MHz): δ 7.27 (q, 1H, J = 2.4 Hz), 6.95 (br s, 1H), 6.27-6.25 (m, 1H), 6.14 (q, 1H, J = 3.2 Hz), 5.95-5.74 (m, 1H), 5.15-5.09 (m, 2H), 4.38-4.31 (m, 2H), 2.96 (t, 2H, J = 5.4 Hz). These spectroscopic data are in good agreement with those reported in the literature.⁶

N-phenyl-3-butenamide (1h)

Following GP1 with aniline (2 equiv, 1.05 mL, 5.8 mmol). The crude product was purified by flash chromatography on silica gel (eluuent: AcOEt/CycloHexane 4:6) to afford 1h in 68% yield (630 mg, 3.9 mmol). White solid. 1H NMR (CDCl₃, 300 MHz): δ 7.56-7.53 (m, 3H), 7.37-7.29 (m, 2H), 7.13 (t, 1H, J = 7.4 Hz), 6.06 (tdd,

1H, J = 7.1, 10.8, 16.0 Hz), 5.37-5.31 (m, 2H), 3.21 (td, 2H, J = 1.2, 7.0 Hz). These spectroscopic data are in good agreement with those reported in the literature.\(^7\)

**N-phenethyl-3-butenamide (1i)**

Following GP1 with phenylethylamine (2 equiv, 1.46 mL, 11.0 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 1i in 40% yield (424 mg, 2.24 mmol).

Pale yellow solid, mp: 63-65 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.35-7.17 (m, 5H), 6.08 (br s, 1H), 5.39 (tdd, 1H, J = 7.1, 10.3, 17.3 Hz), 5.23-5.16 (m, 2H), 3.50 (q, 2H, J = 6.7 Hz), 2.97 (td, 2H, J = 1.3, 7.1 Hz), 2.83 (t, 2H, J = 7.1 Hz). \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 170.4, 138.8, 131.3, 128.7, 128.6, 126.5, 119.8, 41.7, 40.6, 35.6.

IR (cm\(^{-1}\)) \(\gamma\): 3264, 3078, 2930, 1633, 1552.

HRMS (ESI) \(m/z\) calcld for C\(_{12}\)H\(_{15}\)NNaO [M+Na]\(^+\): 212.1046, found 212.1039.

**N,N-dibenzyl-3-butenamide (1j)**

Following GP1 with dibenzylamine (1 equiv, 0.31 mL, 1.6 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 1j in 69% yield (290 mg, 1.1 mmol).

Yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.35-7.03 (m, 10H), 5.96 (tdd, 1H, J = 6.6, 10.2, 16.9), 5.13-4.97 (m, 2H), 4.52 (s, 2H), 4.36 (s, 2H), 3.15 (dt, 2H, J = 6.6, 1.6 Hz). \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 171.5, 137.3, 136.4, 131.7, 129.0, 128.6, 128.4, 127.7, 127.5, 126.4, 117.9, 50.0, 48.2, 38.7. IR (cm\(^{-1}\)) \(\gamma\): 3027, 2919, 1646, 1418, 696.

HRMS (ESI) \(m/z\) calcld for C\(_{18}\)H\(_{19}\)NNaO [M+Na]\(^+\): 288.1359, found 288.1361.

**II-b-Synthesis of allyl-amide 1k**

**N-methoxy-N-methylbut-3-enamide (1k)**

\[
\begin{align*}
\text{HN}\_\text{OMe} &\rightarrow 1) \text{TEA (2 equiv.)} \\
&\text{rt, 2 h} \\
2) \text{CH}_2\text{Cl}_2 &\rightarrow \text{CH}_2\text{Cl}_2 \\
&\text{r.t., overnight}
\end{align*}
\]

A mixture of N,O-dimethylhydroxylamine hydrochloride (1 equiv, 604 mg, 6.2 mmol) and triethylamine (2 equiv, 12.4 mmol, 1.72 mL) in dichloromethane (30 mL) was stirred for 2 hours at room temperature. Then, at 0 °C, but-3-enoyl chloride (1 equiv, 648 mg, 6.2 mmol) freshly prepared [a mixture of thionyl chloride (2 equiv) \(\rightarrow\) Abdou, A.M.; Botros, S.; Hassan, R.A.; Kamel, M.M.; Taber, D.F.; Taher, A.T. *Tetrahedron* 2015, 71, 139.]
and 3-butenoic acid (1 equiv) was stirred for 4 hours at 60 °C, carefully evaporated and immediately used without purification] was added dropwise. The mixture was stirred for 10 minutes at 0 °C, then at r.t. overnight. The reaction was hydrolyzed with a HCl 1N solution, then with a saturated aqueous NaHCO₃ solution and water. The organic layer was extracted with dichloromethane and dried over MgSO₄, filtered and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography (eluent: AcOEt/CycloHexane 6:4) to afford the amide 1k in 54% yield (430 mg, 3.33 mmol). Pale yellow oil. 

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 6.02-5.92 (m, 1H), 5.19-5.18 (m, 1H), 5.16-5.15 (m, 1H), 3.69 (s, 3H), 3.23 (d, J = 6.7 Hz), 3.18 (s, 3H). \]

These spectroscopic data are in good agreement with those reported in the literature.¹

### II-c-Synthesis of allyl-amide 1l

#### Phenyl Allyl Ketone (1l)

Under air atmosphere, to a solution of 1-phenylbut-3-en-1-ol (1 equiv, 300 mg, 2.02 mmol) in acetone (10 mL) at 20 °C was added, using a dropping funnel, a solution of Jones reagent (1.5 mL). After 10 minutes, the time required for change the color of the solution from orange to blue, the mixture was hydrolyzed with water and extracted with diethyl ether. The organic layer was washed with saturated aqueous NaHCO₃, extracted and dried over MgSO₄ and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography (eluent: AcOEt/CycloHexane 1:1) to afford the ketone 1l in 80% yield (235 mg, 1.61 mmol). Colourless oil. 

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 7.97 (d, J = 7.5 Hz), 7.57 (t, J = 7.5 Hz), 7.47 (t, 2H, J = 7.5 Hz), 6.09 (tdd, J = 6.8, 10.4, 17.3 Hz), 5.18-5.27 (m, 2H), 3.76 (td, J = 1.4, 8.2 Hz). \]

These spectroscopic data are in good agreement with those reported in the literature.¹

### III-Procedures and Analytical data of aminated product

#### III-a-Pd(II)-catalyzed direct amination (2a-i, 2l-m, 3a, 4a-e and 5a-d):

In a sealed tube, but-3enoic acid derivative 1 (1 equiv) was dissolved in CH₃CN (0.2 M), and subsequently Pd(OAc)₂ (10 mol%), nucleophile (2 equiv), DIPEA (6 mol%) and BQ (2 equiv) were added to the mixture. Then the reaction was stirred at reflux for 16-48 hours and, after cooling to r.t., was hydrolyzed with a saturated aqueous K₂CO₃ solution and diluted with Et₂O. The organic layer was extracted, dried over MgSO₄, filtered and

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concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: AcOEt/CycloHexane) to afford the aminated compound 2, 3, 4 or 6 depending on the nucleophile used.\(^9\)

**Methyl (E)-(4-(benzylamino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2a)**

Following GP2 with amide 1a (1 equiv, 100 mg, 0.57 mmol) and methyl tosylcarbamate A (2 equiv, 260 mg, 1.13 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2a in 95% yield (219 mg, 0.54 mmol). White solid, mp: 145-146 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta 7.88-7.82 \text{ (m, 2H)}, 7.42-7.30 \text{ (m, 7H)}, 6.91 \text{ (dt, } J = 15.2, 5.3 \text{ Hz)}, 6.03 \text{ (dt, } J = 15.2, 1.7 \text{ Hz)} \), 5.84 (br s, 1H), 4.63 (dd, 2H, \( J = 5.2, 1.7 \text{ Hz} \), 4.55 (dd, 2H, \( J = 5.8, 1.9 \text{ Hz} \)), 3.73 (s, 3H), 2.46 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 164.5, 152.4, 145.0, 138.3, 137.9, 136.0, 129.4, 128.8, 128.6, 128.0, 127.6, 125.4, 54.0, 47.4, 43.8, 21.6. IR (cm\(^{-1}\)) \(\gamma\): 3317, 1737, 1673, 1634, 1440, 1165, 981, 700. HRMS (ESI) m/z calcd for C\(_{20}\)H\(_{22}\)N\(_2\)O\(_5\)S [M+Na]: 425.1142, found 425.1149.

**Methyl (E)-(4-((4-methylbenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2b)**

Following GP2 with amide 1b (1 equiv, 100 mg, 0.53 mmol) and methyl tosylcarbamate A (2 equiv, 242 mg, 1.06 mmol) for 16 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2b in 34% yield (34 mg, 0.082 mmol). Beige solid, mp: 171-172 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.86-7.83 \text{ (m, 2H)}, 7.33-7.28 \text{ (m, 2H)}, 7.22-7.16 \text{ (m, 4H)}, 6.78 \text{ (td, } J = 5.3, 15.3 \text{ Hz)}, 6.00 \text{ (td, } J = 1.7, 15.2 \text{ Hz)} \), 5.82 (br s, 1H), 4.60 (dd, 2H, \( J = 1.7, 5.3 \text{ Hz} \)), 4.48 (d, 2H, \( J = 5.6 \text{ Hz} \)), 3.71 (s, 3H), 2.44 (s, 3H), 2.36 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 164.5, 152.4, 144.9, 143.8, 137.4, 136.0, 134.9, 130.4, 128.6, 128.0, 125.5, 124.7, 43.6, 21.6, 21.1. IR (cm\(^{-1}\)) \(\gamma\): 3292, 2926, 1723, 1634, 1440, 1165, 981, 700. HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{24}\)N\(_2\)O\(_5\)S [M+Na]: 439.1298, found 439.1305.

**Methyl (E)-(4-((4-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2c)**

\(^9\) Sometimes, traces of HBQ (less of 5%) are present in the product.
Following **GP2** with amide **1c** (1 equiv, 100 mg, 0.49 mmol) and methyl tosylcarbamate **A** (2 equiv, 223 mg, 0.97 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford **2c** in 35% yield (73 mg, 0.17 mmol). White solid, mp: 158-159 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.86-7.82 (m, 2H), 7.33-7.24 (m, 4H), 6.92-6.85 (m, 3H), 6.00 (td, 1H, J = 1.7, 15.2 Hz), 5.73 (br s, 1H), 4.61 (dd, 2H, J = 1.7, 5.3 Hz), 4.47 (d, 2H, J = 5.7 Hz), 3.83 (s, 3H), 3.71 (s, 3H), 2.44 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 164.4, 159.2, 129.4, 124.7, 115.1, 114.1, 55.3, 47.4, 43.3, 21.7. IR (cm⁻¹) γ: 3297, 2960, 1744, 1624, 1515, 1358, 1168, 770.

**Methyl (E)-(4-((3-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2d)**

![Structure](image)

Following **GP2** with amide **1d** (1 equiv, 100 mg, 0.49 mmol) and methyl tosylcarbamate **A** (2 equiv, 223 mg, 0.97 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford **2d** in 84% yield (176 mg, 0.4 mmol). White solid, mp: 127-128 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.83-7.80 (m, 2H), 7.31-7.28 (m, 3H), 6.88-6.83 (m, 4H), 6.22 (t, 1H, J = 5.8 Hz), 6.04 (td, 1H, J = 1.7, 15.3 Hz), 4.58 (dd, 2H, J = 1.7, 5.4 Hz), 4.46 (d, 2H, J = 5.7 Hz), 3.79 (s, 3H), 3.68 (s, 3H), 2.42 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 164.7, 159.9, 152.3, 145.0, 139.6, 138.1, 135.9, 129.7, 129.5, 128.5, 125.6, 120.1, 113.5, 113.0, 55.2, 54.0, 47.4, 43.6, 21.6. IR (cm⁻¹) γ: 3292, 2955, 1744, 1627, 1357, 1165, 765. HRMS (ESI) m/z calcd for C₂₁H₂₄N₂O₈S [M+Na]⁺: 455.1247, found 455.1260.

**Methyl (E)-(4-((4-nitrobenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2e)**

![Structure](image)

Following **GP2** with amide **1e** (1 equiv, 100 mg, 0.45 mmol) and methyl tosylcarbamate **A** (2 equiv, 208 mg, 0.98 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford **2e** in 10% yield (16 mg, 0.036 mmol). Pale yellow solid, mp: 182-184 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.14-8.10 (m, 2H), 7.76-7.74 (m, 2H), 7.40-7.38 (m, 2H), 7.24 (d, 2H, J = 8.0 Hz), 6.86 (td, 1H, J = 5.0, 15.2 Hz), 6.05-6.00 (m, 2H), 4.55-4.52 (m, 4H), 3.62 (s, 3H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 164.9, 153.3, 147.4, 145.5, 145.1, 139.4, 135.9, 129.5, 128.5, 128.4, 124.7, 123.9, 54.1, 47.5, 43.0, 21.7. IR (cm⁻¹) γ: 3304, 2921, 1743, 1626, 1517, 1346, 1164, 776. HRMS (ESI) m/z calcd for C₂₀H₂₁N₃O₈S [M+Na]⁺: 470.0992, found 470.1004.

**Methyl (E)-(4-oxo-4-((4-(trifluoromethyl)benzyl)amino)but-2-en-1-yl)(tosyl)carbamate (2f)**

![Structure](image)
Following GP2 with amide 1f (1 equiv, 100 mg, 0.41 mmol) and methyl tosylcarbamate A (2 equiv, 188 mg, 0.82 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2f in 74% yield (142 mg, 0.30 mmol). White solid, mp: 173-174 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.76-7.74 (m, 2H), 7.51-7.52 (m, 2H), 7.36-7.33 (m, 2H), 7.24-7.22 (m, 2H), 6.83 (dt, 1H, J = 15.3, 5.2 Hz), 5.94 (dt, 1H, J = 15.2, 1.6 Hz), 5.91 (br s, 1H), 4.52 (dd, 2H, J = 5.2, 1.7 Hz), 4.49 (d, 2H, J = 6.0 Hz), 3.62 (s, 3H), 2.35 (s, 3H). 13C NMR (CDCl₃, 100 MHz): δ 164.8, 152.3, 145.0, 142.0, 138.9, 135.9, 129.7 (J = 32.0 Hz), 129.5, 128.5, 128.0, 125.7 (J = 3.7 Hz), 125.0, 122.9 (J = 272.0 Hz), 54.1, 47.4, 43.2, 21.6. 19F NMR (CDCl₃, 282 MHz): δ -62.53. IR (cm⁻¹) γ: 3316, 2925, 1737, 1676, 1636, 1361, 1169, 911, 733. HRMS (ESI) m/z calcd for C₂₁H₂₁F₂N₂O₃S [M+Na]⁺: 493.1015, found 493.1012.

Methyl (E)-{4-[(furan-2-yl)methyl]amino}-4-oxobut-2-en-1-yl)(tosyl)carbamate (2g)

Following GP2 with amide 1h (1 equiv, 100 mg, 0.60 mmol) and methyl tosylcarbamate A (2 equiv, 277 mg, 1.2 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 7:3) to afford 2g in 46% yield (109 mg, 0.28 mmol). Brown oil. 1H NMR (CDCl₃, 400 MHz): δ 7.73-7.72 (m, 2H), 7.28 (dd, 1H, J = 0.8, 1.9 Hz), 7.24-7.22 (m, 2H), 6.78 (td, 1H, J = 5.2, 15.3 Hz), 6.25 (dd, 1H, J = 1.9, 3.2 Hz), 6.19-6.17 (m, 1H), 5.96 (br s, 1H), 5.93 (td, 1H, J = 1.7, 15.3 Hz), 4.51 (dd, 2H, J = 1.7, 5.3 Hz), 4.42 (d, 2H, J = 5.5 Hz), 3.61 (s, 3H), 2.35 (s, 3H). 13C NMR (CDCl₃, 100 MHz): δ 164.6, 152.4, 145.0, 142.3, 138.5, 138.5, 129.5, 128.5, 125.2, 110.5, 107.7, 54.0, 47.4, 36.6, 21.7. IR (cm⁻¹) γ: 3304, 2956, 1747, 1628, 1357, 1165, 759. HRMS (ESI) m/z calcd for C₁₈H₁₉FN₂O₆S [M+Na]⁺: 415.0934, found 415.0938.

Methyl (E)-{4-oxo-4-(phenylamino)but-2-en-1-yl}(tosyl)carbamate (2h)

Following GP2 with amide 1h (1 equiv., 50 mg, 0.31 mmol) and methyl tosylcarbamate A (2 equiv, 142 mg, 0.62 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2h in 90% yield (52 mg, 0.14 mmol). Brown solid, mp: 153-155 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.78-7.75 (m, 2H), 7.62 (br s, 1H), 7.49 (d, 2H, J = 8.0 Hz), 7.26-7.18 (m, 4H), 7.04 (t, 1H, J = 7.4 Hz), 6.89 (td, 1H, J = 5.2, 15.2 Hz), 6.14 (td, 1H, J = 1.7, 15.2 Hz), 4.56 (dd, 2H, J = 1.7, 5.1 Hz), 3.63 (s, 3H), 2.34 (s, 3H). 13C NMR (CDCl₃, 100 MHz): δ 162.9, 152.4, 145.0, 139.2, 136.3, 135.9, 129.5, 129.0, 128.5, 126.0,
124.4, 119.9, 54.1, 47.5, 21.6. IR (cm⁻¹) γ: 3353, 2916, 1689, 1536, 1440, 1254, 1185, 1080. HRMS (ESI) m/z calcd for C₁₉H₂₀N₂NaO₅S [M+Na]⁺: 411.0985, found 411.0975.

Methyl (E)-(4-oxo-4-(phenethylamino)-2-en-1-yl)(tosyl)carbamate (2i)

Following GP2 with amide 1i (1 equiv, 100 mg, 0.53 mmol) and methyl tosylcarbamate A (2 equiv, 243 mg, 1.01 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2i in 41% yield (90 mg, 0.22 mmol). White solid, mp: 145-147 °C. \(^1\)H NMR (CDCl₃, 400 MHz): δ 7.76-7.73 (m, 2H), 7.27-7.12 (m, 7H), 6.74 (td, 1H, J = 5.3, 15.3 Hz), 5.85 (td, 1H, J = 1.7, 15.3 Hz), 5.48 (br s, 1H), 5.40 (dd, 2H, J = 1.7, 5.3 Hz), 3.61 (s, 3H), 3.56-3.50 (m, 2H), 2.78 (t, 2H, J = 7.0 Hz), 2.36 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz): δ 164.7, 152.4, 144.9, 138.7, 137.9, 135.9, 129.4, 128.8, 128.7, 128.5, 126.6, 125.6, 54.0, 47.3, 40.7, 35.6, 21.7. IR (cm⁻¹) γ: 3309, 3026, 2960, 1745, 1627, 1546, 1398, 1128, 907. HRMS (ESI) m/z calcd for C₂₁H₂₄N₂NaO₅S [M+Na]⁺: 439.1298, found 439.1311.

Methyl (E)-(4-oxo-4-phenylbut-2-en-1-yl)(tosyl)carbamate (2l)

Following GP2 with phenyl allyl ketone 1l (1 equiv, 100 mg, 0.68 mmol) and methyl tosylcarbamate A (2 equiv, 309 mg, 1.35 mmol) for 24 hours. The residue was taken up in DCM and treated with an equal volume of 1N KOH for 15 minutes. After decantation and phase separation, the organic layer was dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2l in 40% yield (102 mg, 0.27 mmol). Brown oil. \(^1\)H NMR (CDCl₃, 400 MHz): δ 7.95 (td, 2H, J = 1.8, 8.7 Hz), 7.93-7.87 (m, 2H), 7.62-7.57 (m, 1H), 7.52-7.49 (m, 2H), 7.37-7.31 (m, 2H), 7.13 (td, 1H, J = 1.8, 15.5 Hz), 7.02 (td, 1H, J = 6.0, 15.5 Hz), 4.76 (dd, 2H, J = 2.0, 6.2 Hz), 3.74 (s, 3H), 2.45 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz): δ 189.7, 152.4, 145.1, 141.8, 137.3, 136.0, 133.1, 129.5, 128.7, 128.6, 126.8, 125.6, 54.0, 47.3, 35.6, 21.7. IR (cm⁻¹) γ: 2958, 1737, 1676, 1359, 1169, 907. HRMS (ESI) m/z calcd for C₁₉H₁₉NNaO₅S [M+Na]⁺: 396.0876, found 396.0884.

Methyl (E)-(4-((N-(methoxycarbonyl)-4-methylphenyl)sulfonamido)but-2-enoate (2m)

Following GP2 with methyl but-3-enoate (1 equiv, 50 mg, 0.5 mmol) and methyl tosylcarbamate A (2 equiv, 228 mg, 0.99 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 2m in 93% yield (137 mg, 0.42 mmol). Beige solid, mp: 132-133 °C. \(^1\)H NMR
(CDCl₃, 400 MHz): δ 7.86-7.84 (m, 2H), 7.36-7.34 (m, 2H), 6.94 (td, 1H, J = 5.4, 15.7), 6.04 (td, 1H, J = 1.7, 15.7 Hz), 4.62 (dd, 2H, J = 1.7, 3.5 Hz), 3.77 (s, 3H), 3.73 (s, 3H), 2.47 (s, 3H). 

1H NMR (CDCl₃, 400 MHz): δ 7.72-7.69 (m, 2H), 7.30-7.21 (m, 7H), 6.77 (dt, 1H, J = 15.2, 5.2 Hz), 5.88 (dt, 1H, J = 15.2, 1.7 Hz), 5.69 (br s, 1H), 4.51 (dd, 2H, J = 1.7, 5.2 Hz), 4.43 (d, 2H, J = 5.7 Hz), 2.36 (s, 3H), 2.24 (s, 3H).

13C NMR (CDCl₃, 100 MHz): δ 164.2, 158.5, 137.8, 137.7, 135.6, 135.0, 134.5, 128.7, 127.9, 127.6, 127.1, 126.7, 125.3, 121.1, 143.8, 39.2. IR (cm⁻¹): υ: 3312, 1744, 1625, 1325, 1185, 973, 752.


(E)-N-benzyl-4-(N-tosylacetamido)but-2-enamide (3a)

Following GP2 with amide 1a (1 equiv, 100 mg, 0.57 mmol) and N-tosylacetamide B (2 equiv, 261 mg, 1.14 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 3a in 61% yield (133 mg, 0.34 mmol). Beige solid, mp: 161-162 °C.

(E)-N-benzyl-4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)but-2-enamide (4a)

Following GP2 with amide 1a (1 equiv, 100 mg, 0.57 mmol) and saccharin C (2 equiv, 208 mg, 1.14 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 4a in 40% yield (80 mg, 0.02 mmol). White solid, mp: 149-150 °C.

(E)-4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-N-(4-methylbenzyl)but-2-enamide (4b)

Following GP2 with amide 1b (1 equiv, 100 mg, 0.53 mmol) and saccharin C (2 equiv, 193 mg, 1.05 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 4b in 33% yield (64 mg, 0.17 mmol). White solid, mp: 171-172 °C.

1H NMR (CDCl₃, 400 MHz): δ 8.00-7.98 (m, 1H), 7.87-7.75 (m, 3H), 7.27-7.17 (m, 5H), 6.84 (td, 1H, J = 5.5, 15.3 Hz), 6.01 (td, 1H, J = 1.7, 15.2 Hz), 5.75 (br s, 1H), 4.44-4.40 (m, 4H). 

13C NMR (CDCl₃, 100 MHz): δ 164.2, 158.5, 137.8, 137.7, 135.6, 135.0, 134.5, 128.7, 127.9, 127.6, 127.1, 126.7, 125.3, 121.1, 43.8, 39.2. IR (cm⁻¹): υ: 3312, 1744, 1625, 1325, 1185, 973, 752. HRMS (ESI) m/z calcd for C₁₈H₁₆N₂NaO₄S [M+Na]⁺: 379.0723, found 379.0709.
7.98 (m, 1H), 7.87-7.77 (m, 3H), 7.10-7.04 (m, 4H), 6.83 (td, 1H, J = 5.4, 15.2 Hz), 5.99 (td, 1H, J = 1.7, 15.2 Hz), 5.66 (br s, 1H), 4.41 (dd, 2H, J = 1.7, 5.4 Hz), 4.37 (d, 2H, J = 5.6 Hz), 2.25 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 164.2, 158.5, 137.7, 137.3, 135.5, 135.0, 134.7, 134.5, 129.4, 127.9, 127.1, 126.8, 125.3, 121.1, 43.6, 39.2, 21.1. IR (cm$^{-1}$) $\gamma$: 3291, 2922, 1731, 1621, 1334, 1186. HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$: 393.0879, found 393.0876.

$(E)$-4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-N-(4-methoxybenzyl)but-2-enamide (4c)

Following GP2 with amide 1c (1 equiv, 100 mg, 0.49 mmol) and saccharin C (2 equiv, 178 mg, 0.97 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 4c in 57% yield (106 mg, 0.27 mmol). White solid, mp: 164-165 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.09 (ddd, 1H, J = 0.7, 1.5, 7.2 Hz), 7.97-7.85 (m, 3H), 7.23-7.20 (m, 2H), 6.93 (td, 1H, J = 5.4, 15.3 Hz), 6.88-6.85 (m, 2H), 6.08 (td, 1H, J = 1.7, 15.2 Hz), 5.74 (br s, 1H), 4.51 (dd, 2H, J = 1.7, 5.5 Hz), 4.44 (d, 2H, J = 5.6 Hz), 3.80 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 164.1, 159.1, 158.5, 137.7, 135.5, 135.0, 134.5, 129.9, 129.3, 127.1, 126.7, 125.3, 121.2, 114.1, 55.3, 43.3, 39.2. IR (cm$^{-1}$) $\gamma$: 3293, 2933, 1734, 1513, 1182, 909, 730. HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$: 409.0829, found 409.0836.

$(E)$-4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-N-(3-methoxybenzyl)but-2-enamide (4d)

Following GP2 with amide 1d (1 equiv, 100 mg, 0.48 mmol) and saccharin C (2 equiv, 178 mg, 0.97 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 4d in 82% yield (154 mg, 0.4 mmol). White solid, mp: 138-140 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.11-8.02 (m, 1H), 7.95-7.87 (m, 3H), 7.25 (dd, 1H, J = 7.5, 9.0 Hz), 6.93 (td, 1H, J = 5.4, 15.3 Hz), 6.82-6.84 (m, 3H), 6.10 (td, 1H, J = 1.7, 15.2 Hz), 5.80 (br s, 1H), 4.52 (dd, 2H, J = 1.7, 5.4 Hz), 4.48 (d, 2H, J = 5.7 Hz), 3.80 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 164.2, 159.9, 158.5, 139.3, 137.8, 135.7, 135.0, 134.5, 129.8, 127.1, 126.7, 125.4, 121.0, 120.2, 113.4, 113.2, 55.2, 43.8, 39.2. IR (cm$^{-1}$) $\gamma$: 3287, 2921, 1731, 1625, 1331, 1213, 1013. HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$: 409.0829, found 409.0840.

$(E)$-4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-N-(4-nitrobenzyl)but-2-enamide (4e)
Following GP2 with amide 1e (1 equiv, 65 mg, 0.29 mmol) and saccharin C (2 equiv, 108 mg, 0.59 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 4e in 30% yield (35 mg, 0.09 mmol). Beige solid, mp: 168-169 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.11-8.08 (m, 2H), 8.00 (ddd, 1H, J = 7.3, 1.4, 0.7 Hz), 7.89-7.77 (m, 3H), 7.39-7.35 (m, 2H), 6.88 (td, 1H, J = 5.4, 15.3 Hz), 6.07 (td, 1H, J = 1.7, 15.3 Hz), 5.93 (br s, 1H), 4.52 (d, 2H, J = 6.3 Hz), 4.44 (dd, 2H, J = 1.7, 5.4 Hz).

Following GP2 with amide 1b (1 equiv, 100 mg, 0.53 mmol) and N-tert-butanesulfinyl carbamate D (2 equiv, 204 mg, 1.14 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 5a in 47% yield (93 mg, 0.26 mmol). Yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.27 (m, 5H), 6.80 (td, 1H, J = 5.5, 15.4 Hz), 6.08 (br s, 1H), 5.95 (td, 1H, J = 1.6, 15.3), 4.46 (d, 2H, J = 5.7 Hz), 4.12 (ddd, 1H, J = 1.7, 5.4, 16.9 Hz), 3.94 (ddd, 1H, J = 1.7, 5.4, 16.9 Hz), 3.77 (s, 3H).

Methyl (E)-(4-(benzylamino)-4-oxobut-2-en-1-yl)(tert-butylsulfinyl)carbamate (5a)

Following GP2 with amide 1a (1 equiv, 100 mg, 0.57 mmol) and N-tert-butanesulfinyl carbamate D (2 equiv, 204 mg, 1.14 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 5b in 27% yield (51 mg, 0.14 mmol). Yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.12-7.05 (m, 4H), 6.73 (ddd, 1H, J = 5.4, 6.1, 15.4 Hz), 5.83 (td, 1H, J = 1.6, 15.3 Hz), 5.73 (br s, 1H), 4.37 (d, 2H, J = 5.7 Hz), 4.04 (ddd, 1H, J = 1.5, 6.1, 16.9 Hz), 3.87 (ddd, 1H, J = 1.7, 5.5, 16.9 Hz), 3.70 (s, 3H).

Methyl (E)-(tert-butylsulfinyl)(4-((4-methylbenzyl)amino)-4-oxobut-2-en-1-yl)carbamate (5b)
Methyl (E)-(tert-butylsulfinyl)(4-((4-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)carbamate (5c)

Following GP2 with amide 1c (1 equiv, 100 mg, 0.49 mmol) and N-tert-butanesulfonfyl carbamate D (2 equiv, 174 mg, 0.97 mmol) for 30 hours. The crude product was purified by flash chromatography on silica gel (elu: AcOEt/CycloHexane 1:1) to afford 5c in 16% yield (29 mg, 0.08 mmol). Yellow oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.14 (d, 2H, \(J = 8.7\) Hz), 6.79 (d, 2H, \(J = 8.7\) Hz), 6.72 (td, 1H, \(J = 5.7, 15.3\) Hz), 5.83 (td, 1H, \(J = 1.7, 15.2\) Hz), 5.68 (br s, 1H), 4.35 (d, 2H, \(J = 5.7\) Hz), 4.08-4.01 (m, 1H), 3.87 (ddd, 1H, \(J = 1.7, 5.4, 16.9\) Hz), 3.72 (s, 3H), 3.70 (s, 3H), 1.14 (s, 9H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 164.7, 159.1, 155.4, 139.3, 130.0, 129.3, 125.8, 114.1, 60.2, 55.3, 53.6, 43.3, 39.1, 22.5. IR (cm\(^{-1}\)) \(\gamma\): 2927, 1717, 1513, 1250, 1089, 909, 731. HRMS (ESI) \(m/z\) calcd for C\(_{18}\)H\(_{26}\)KN\(_2\)O\(_5\)S [M+K]\(^+\): 421.1194, found 421.1199.

Methyl (E)-(tert-butylsulfinyl)(4-((3-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)carbamate (5d)

Following GP2 with amide 1d (1 equiv, 100 mg, 0.49 mmol) and N-tert-butanesulfonfyl carbamate D (2 equiv, 175 mg, 0.97 mmol) for 48 hours. The crude product was purified by flash chromatography on silica gel (elu: AcOEt/CycloHexane 1:1) to afford 5d in 50% yield (93 mg, 0.24 mmol). Pale brown oil \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.20-7.15 (m, 1H), 6.80-6.69 (m, 4H), 5.90 (br s, 1H), 5.86 (td, 1H, \(J = 1.6, 15.3\) Hz), 4.38 (d, 2H, \(J = 5.7\) Hz), 4.05 (ddd, 1H, \(J = 1.5, 6.1, 16.9\) Hz), 3.87 (ddd, 1H, \(J = 1.7, 5.4, 16.9\) Hz), 3.72 (s, 3H), 3.70 (s, 3H), 1.14 (s, 9H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 164.8, 159.8, 155.4, 139.5, 139.4, 129.7, 125.7, 120.2, 113.5, 113.0, 60.2, 55.2, 53.6, 43.7, 39.1, 22.5. IR (cm\(^{-1}\)) \(\gamma\): 2927, 1717, 1675, 1634, 1442, 1264, 907, 728. HRMS (ESI) \(m/z\) calcd for C\(_{18}\)H\(_{26}\)KN\(_2\)O\(_5\)S [M+K]\(^+\): 421.1194, found 421.1203.

III-b-Pd(II)-catalyzed direct acyloxylation (6a-k, 6m): General procedure (GP3)

- Further optimizations
A solution of LiOH·H₂O (2 equiv), RCOOH (x equiv) in CH₃CN was heated at 40 °C for 20-24 h. Then BQ (2 equiv), Pd(OAc)₂ (10 mol%), and CH₃CN (0.2 M) were added. The resulting mixture was stirred for 15 minutes at r.t. and the corresponding but-3-enoic acid derivatives 1 (1 equiv) was added. The reaction was stirred at 40°C until the completion of the reaction. After cooling to r.t., the mixture was filtered through a SiO₂ pad and washed with Et₂O. NaOH (2 M) was added and the middle was stirred for 15 minutes. The organic phase was hydrolyzed with H₂O, extracted with Et₂O, dried over MgSO₄, filtered and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding pivaloylated product 6.

**(E)-4-(benzylamino)-4-oxobut-2-en-1-yl pivalate (6a)**

Following GP3 with 1a (1 equiv, 300 mg, 1.70 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6a in 98% yield (458 mg, 1.67 mmol). White solid, mp: 66-68 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.26 (m, 5H), 6.90-6.84 (m, 1H), 6.15 (br s, 1H), 6.02 (d, 1H, J = 15.4 Hz), 4.69 (dd, 2H, J = 4.7, 1.8 Hz), 4.50 (d, 2H, J = 5.7 Hz), 1.23 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 178.0, 165.0, 138.1, 137.9, 128.8, 128.0, 127.7, 124.3, 62.9, 43.8, 38.9, 27.3. IR (cm⁻¹): 3247, 2968, 1727, 1678, 1278, 1159. HRMS (ESI) m/z calc'd: C₁₈H₂₁NNaO₃ [M+Na]⁺: 298.1419, found 298.1414.

**(E)-4-((4-Methylbenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6b)**

C₂₇H₂₅NO₃
M.W.: 289,1678
Following GP3 with amide 1b (1 equiv, 100 mg, 0.53 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6b in 50% yield (75 mg, 0.26 mmol). White solid, mp: 144-145 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.09-7.03 (m, 4H), 6.79-6.72 (m, 1H), 6.10 (br s, 1H), 5.92 (td, 2H, $J = 2.0, 15.6$ Hz), 4.60-4.57 (m, 2H), 4.36-4.34 (m, 2H), 2.24 (s, 3H), 1.13 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 177.9, 164.8, 137.6, 137.3, 134.9, 129.3, 127.9, 124.3, 62.8, 43.5, 38.8, 27.2, 21.1. IR (cm$^{-1}$) $\gamma$: 3242, 2971, 1733, 1673, 1622, 1281, 1142. HRMS (ESI) $m/z$ calcd for C$_{17}$H$_{23}$NNaO$_3$ [M+Na]$^+$: 312.1570, found 312.1570.

$^{(E)}$-4-((4-Methoxybenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6c)

Following GP3 with amide 1c (1 equiv, 300 mg, 1.5 mmol) for 23 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6c in 70% yield (306 mg, 1.00 mmol). Brown solid, mp: 125-127 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.26-7.23 (m, 2H), 6.93-6.87 (m, 3H), 5.99 (dt, 1H, $J = 1.6, 15.2$ Hz), 5.82 (br s, 1H), 4.73 (dd, 2H, $J = 2.0, 4.4$ Hz), 4.47 (dd, 2H, $J = 1.6, 5.6$ Hz), 3.82 (s, 3H), 1.24 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 177.9, 164.7, 159.1, 137.9, 129.9, 129.3, 124.1, 114.1, 62.7, 55.3, 43.3, 38.8, 27.2. IR (cm$^{-1}$) $\gamma$: 3371, 2961, 1712, 1674, 1513, 1245, 1161. HRMS (ESI) $m/z$ calcd for C$_{17}$H$_{23}$NNaO$_4$ [M+Na]$^+$: 328.1519, found 328.1518.

$^{(E)}$-4-((3-methoxybenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6d)

Following GP3 with amide 1d (1 equiv, 100 mg, 0.48 mmol) for 23 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6d in 62% yield (91 mg, 0.20 mmol). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.20-7.16 (m, 1H), 6.85-6.73 (m, 4H), 5.92 (td, 1H, $J = 1.9, 15.3$ Hz), 5.84 (br s, 1H), 4.63 (dd, 2H, $J = 1.7, 4.7$ Hz), 4.41 (d, 2H, $J = 5.7$ Hz), 3.72 (s, 3H), 1.15 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 177.9, 164.7, 159.9, 139.5, 137.9, 129.8, 124.1, 120.1, 113.6, 113.0, 62.8, 55.2, 43.7, 38.8, 27.2. IR (cm$^{-1}$) $\gamma$: 3271, 2969, 1729, 1675, 1513, 1245, 1161. HRMS (ESI) $m/z$ calcd for C$_{17}$H$_{23}$NNaO$_4$ [M+Na]$^+$: 328.1519, found 328.1521.

$^{(E)}$-4-((4-nitrobenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6e)
Following GP3 with amide 1e (1 equiv, 100 mg, 0.45 mmol) for 24 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6e in 75% yield (109 mg, 0.34 mmol). White solid, mp: 112-113 °C. 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz): \delta 8.10-8.06 (m, 2H), 7.37 (dd, 2H, \textit{J} = 2.4, 8.7 Hz), 6.84 (ddd, 1H, \textit{J} = 15.1, 6.2, 3.4 Hz), 6.15 (br s, 1H), 6.02-5.94 (m, 1H), 4.65 (dd, 2H, \textit{J} = 1.9, 4.1 Hz), 4.54 (dd, 2H, \textit{J} = 2.8, 6.5 Hz), 1.16 (s, 9H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 100 MHz): \delta 177.8, 165.1, 147.3, 145.7, 138.8, 128.3, 123.8, 123.5, 62.7, 42.9, 38.8, 27.2. IR (cm}^{-1}): 3267, 2974, 1730, 1673, 1633, 1518, 1345, 1145. \]

HRMS (ESI) \textit{m/z} calcd for C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}NaO\textsubscript{5} [M+Na]\textsuperscript{+}: 343.1264, found 343.1257.

\[ (E)-4-\text{oxo-4-((4-(trifluoromethyl)benzyl)amino)but-2-en-1-yl pivalate (6f)} \]

Following GP3 with amide 1f (1 equiv, 300 mg, 1.23 mmol) for 23 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6f in 91% yield (382 mg, 1.1 mmol). Orange viscous oil. 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz): \delta 7.50-7.48 (m, 2H), 7.32-7.30 (m, 2H), 6.82 (dt, 1H, \textit{J} = 15.4, 4.7 Hz), 6.19 (br s, 1H), 5.95 (dt, 1H, \textit{J} = 15.3, 1.9 Hz), 4.63 (dd, 2H, \textit{J} = 1.9, 4.7 Hz), 4.46 (d, 2H, \textit{J} = 6.0 Hz), 1.14 (s, 9H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 100 MHz): \delta 177.9, 165.1, 142.0, 138.5, 129.8 (\textit{J} = 31.5 Hz), 127.9, 125.6 (\textit{J} = 3.6 Hz), 124.0 (\textit{J} = 273.5 Hz), 123.7, 62.7, 43.4, 38.8, 27.1. \]

\[ \text{\textsuperscript{19}F NMR (CDCl}_3, 282 MHz): \delta -62.53. \]

IR (cm}^{-1}): 3276, 3076, 1728, 1676, 1634, 1324, 1158, 906, 728. HRMS (ESI) \textit{m/z} calcd for C\textsubscript{17}H\textsubscript{20}F\textsubscript{3}NNaO\textsubscript{3} [M+Na]\textsuperscript{+}: 366.1287, found 366.1285.

\[ (E)-4-\text{oxo-4-((Furan-2-ylmethyl)amino)but-2-en-1-yl pivalate (6g)} \]

Following GP3 with amide 1g (1 equiv, 150 mg, 0.9 mmol) for 22 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6g in 35% yield (80 mg, 0.30 mmol). Yellow solid, mp: 125 °C. 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz): \delta 7.29 (dd, 1H, \textit{J} = 0.8, 2.0 Hz), 6.81 (ddd, 1H, \textit{J} = 4.4, 4.8, 15.2 Hz), 6.25 (dd, 1H, \textit{J} = 2.0, 3.2 Hz), 6.18-6.17 (m, 1H), 5.92 (td, 1H, \textit{J} = 1.6, 15.2 Hz), 5.90 (br s, 1H), 4.63 (dd, 2H, \textit{J} = 1.6, 4.8 Hz), 4.44 (d, 2H, \textit{J} = 5.6 Hz), 1.16 (s, 9H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 100 MHz): \delta 177.8, 164.6, 150.9, 142.3, 138.0, 123.9, 110.5, 107.7, 62.7, 38.8, 36.5, 27.2. IR (cm}^{-1}): 3230, 2966, 1730, 1672, 1626, 1151, 752. HRMS (ESI) \textit{m/z} calcd for C\textsubscript{14}H\textsubscript{19}NNaO\textsubscript{4} [M+Na]\textsuperscript{+}: 288.1206, found 288.1201.

\[ (E)-4-Oxo-4-(phenylamino)but-2-en-1-yl pivalate (6h) \]
Following GP3 with amide 1h (1 equiv, 200 mg, 1.24 mmol) for 20 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/Cyclohexane 1:1) to afford 6h in 44% yield (142 mg, 0.54 mmol). Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.78 (br s, 1H), 7.49 (d, 2H, $J = 8.0$ Hz), 7.22 (t, 2H, $J = 7.9$ Hz), 7.03 (t, 1H, $J = 7.4$ Hz), 6.88 (td, 1H, $J = 4.8$, 15.3 Hz), 6.10 (td, 1H, $J = 1.9$, 15.3 Hz), 4.64 (dd, 2H, $J = 1.9$, 4.8 Hz), 1.15 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 177.9, 163.2, 138.7, 137.8, 129.0, 124.9, 124.6, 120.1, 62.8, 38.9, 27.2. IR (cm$^{-1}$): 3269, 2927, 1730, 1678, 1642, 1543, 1442, 1149, 754. HRMS (ESI) $m/z$ calcd for C$_{15}$H$_{19}$NNaO$_3$ [M+Na]$^+$: 284.1257, found 284.1267.

(E)-4-Oxo-4-(phenethylamino)but-2-en-1-yl pivalate (6i)

Following GP3 with amide 1i (1 equiv, 150 mg, 0.8 mmol) for 22 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/Cyclohexane 1:1) to afford 6i in 83% yield (191 mg, 0.66 mmol). Pale yellow viscous oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.26-7.12 (m, 5H), 6.76 (dt, 1H, $J = 15.4$, 4.9 Hz), 5.83 (dt, 1H, $J = 15.4$, 1.8 Hz), 5.46 (s, 1H), 4.62 (dd, 2H, $J = 1.9$, 4.9 Hz), 3.56-3.51 (m, 2H), 2.79 (t, 2H, $J = 6.9$ Hz), 1.15 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 177.8, 164.9, 138.7, 137.5, 128.8, 128.7, 126.6, 124.4, 62.8, 40.7, 35.6, 33.9, 27.2. IR (cm$^{-1}$): 3283, 2931, 1730, 1676, 1632, 1151, 738. HRMS (ESI) $m/z$ calcd for C$_{17}$H$_{23}$KNO$_3$ [M+K]$^+$: 328.1310, found 328.1312.

(E)-4-(Dibenzylamino)-4-oxobut-2-en-1-yl pivalate (6j)

Following GP3 with amide 1j (1 equiv, 100 mg, 0.4 mmol) for 22 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/Cyclohexane 4:6) to afford 6j in 60% yield (81 mg, 0.22 mmol). Yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.44-7.25 (m, 8H), 7.19 (d, 2H, $J = 7.0$ Hz), 7.07 (dt, 1H, $J = 15.2$, 4.5 Hz), 6.49 (dt, 1H, $J = 15.1$, 1.9 Hz), 4.76 (dd, 2H, $J = 4.5$, 1.9 Hz), 4.71 (s, 2H), 4.54 (s, 2H), 1.15 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 177.7, 166.5, 140.1, 137.1, 136.4, 129.0, 128.6, 128.4, 127.7, 127.5, 126.4, 121.0, 62.9, 50.0, 48.9, 38.8, 27.1. IR (cm$^{-1}$): 3030, 2971, 2359, 1730, 1676, 1625, 1426, 1362, 1278, 1150, 960. HRMS (ESI) $m/z$ calcd for C$_{23}$H$_{27}$NNaO$_3$ [M+Na]$^+$: 388.1883, found 388.1896.

(E)-4-(methoxy(methyl)amino)-4-oxobut-2-en-1-yl pivalate (6k)
Following GP3 with amide 1k (1 equiv, 60 mg, 0.46 mmol) for 26 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 6k in 48% yield (51 mg, 0.22 mmol). Yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 6.96-6.91 (m, 1H), 6.58 (d, 1H, $J = 15.6$ Hz), 4.75-4.74 (m, 2H), 3.68 (s, 3H), 3.23 (s, 3H), 1.22 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 177.8, 166.1, 140.2, 119.6, 63.1, 61.8, 39.0, 32.5, 27.3. IR (cm$^{-1}$): 2971, 1730, 1669, 1633, 1364. HRMS (ESI) m/z calcd for C$_{15}$H$_{19}$NNaO$_4$ [M+Na]$^+$: 252.1212, found 252.1206.

Methyl (E)-4-(pivaloyloxy)but-2-enoate (6m)

Following GP3 with methyl 3-butenoleate 1m (1 equiv, 100 mg, 0.99 mmol) for 22 hours. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 4:6) to afford 6m in 81% yield (163 mg, 0.81 mmol). Yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.05-6.88 (m, 1H), 6.03 (dt, $J = 15.8$, 2.0 Hz, 1H), 4.74 (dd, $J = 4.4$, 2.0 Hz, 2H), 3.77 (m, 3H), 1.24 (dd, $J = 7.0$, 2.0 Hz, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 177.7, 166.3, 141.9, 121.3, 62.4, 51.7, 38.8, 27.0. IR (cm$^{-1}$): 2972, 2874, 1728, 1664, 1476, 1367, 1315, 1146. HRMS (ESI) m/z calcd for C$_{10}$H$_{16}$NaO$_4$ [M+Na]$^+$: 223.0941, found 223.0935.

III-c-Pd(0)-catalyzed amination (7a): general procedure (GP4)

A sealed tube was charged with the amide 6a (1 equiv, 50 mg, 0.18 mmol) and CH$_3$CN (900 μL, 0.2 M). Then, Pd(OAc)$_2$ (10 mol%, 4 mg, 0.018 mmol), (+)-BINAP (20 mol%, 22.4 mg, 0.036 mmol), Phthalimide (3 equiv, 79.5 mg, 0.54 mmol) were added to the mixture. DIPEA was added last via a syringe (11.5 equiv, 352 μL, 2.07 mmol) and the mixture was stirred at reflux for the time required to complete the reaction (24 h). The solution was filtered through a small plug of silica gel, washed with AcOEt and concentrated at reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 7a in 83% yield (48 mg, 0.15 mmol).

III-d-Sequential Pd(II) / Pd(0) catalyzed amination (7a-d, 7g-i): General procedure (GP5)

a. LiOH monohydrate (2 equiv) PivOH (10 equiv)

b. Pd(OAc)$_2$ (10 mol%) BQ (2 equiv) CH$_3$CN, 40 °C, 8 h

c. Phthalimide (3 equiv) DIPEA (11.5 equiv) (+)-BINAP (20 mol%) 70 °C, 18 h
A sealed tube was charged with LiOH·H₂O (2 equiv) and tBuCOOH (10 equiv) and was heated at 40 °C for 10 minutes. Then, BQ (2 equiv), Pd(OAc)₂ (10 mol%) and CH₂CN (0.2 M) were added. The mixture was stirred for 15 minutes at r.t., and then the corresponding amide (1a-d, 1g-i) (1 equiv) was added. The mixture was stirred at 40 °C for 8 hours. The completion of the reaction was monitored by TLC, and then DIPEA (11.5 equiv), Phthalimide (3 equiv) and (+)-BINAP (20 mol%) were added and the mixture was stirred at 70 °C for 18 hours. After cooling to r.t., the mixture was filtered through a SiO₂ pad and washed with AcOEt (20 mL for two times), then concentrated at reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding aminated compound (7a-d, 7g-i).

(E)-N-benzyl-4-(1,3-dioxoisindolin-2-yl)but-2-enamide (7a)

Following GPS with amide 1a (1 equiv, 100 mg, 0.57 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 7a in 90% yield (142 mg, 0.44 mmol). White solid, mp: 184-185 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ 8.39 (t, 1H, J = 5.7 Hz), 7.92-7.85 (m, 4H), 7.29-7.27 (m, 2H), 7.22-7.20 (m, 2H), 6.68 (dt, 1H, J = 15.4, 4.6 Hz), 5.96 (dt, 1H, J = 15.5, 1.8 Hz), 4.33 (dd, 2H, J = 4.6, 1.9 Hz), 4.28 (d, 2H, J = 5.9 Hz). ¹³C NMR (DMSO-d₆, 100 MHz): δ 167.4, 164.0, 139.1, 136.3, 134.5, 131.6, 128.3, 127.4, 126.8, 124.4, 123.2, 42.1, 38.0. IR (cm⁻¹): 3282, 1771, 1701, 1629, 977, 720. HRMS (ESI) m/z calcd for C₁₉H₁₆N₂O₃ [M+Na]^+: 343.1059, found 343.1053.

(E)-4-(1,3-dioxoisindolin-2-yl)-N-(4-methylbenzyl)but-2-enamide (7b)

Following GPS with amide 1b (1 equiv, 100 mg, 0.52 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 7b in 22% (38 mg, 0.11 mmol). Pale yellow solid, mp: 180-182 °C. ¹H NMR (CDCl₃, 300 MHz) δ 7.83-7.75 (m, 2H), 7.69-7.62 (m, 2H), 7.12-7.03 (m, 4H), 6.80-6.74 (m, 1H), 5.82 (dt, 1H, J = 15.3, 1.6 Hz), 5.58 (brs, 1H), 4.39-4.32 (m, 4H), 2.25 (d, 3H, J = 4.3 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 167.6, 164.5, 137.4, 136.8, 134.8, 134.2, 132.0, 129.4, 127.9, 125.7, 123.5, 43.6, 38.2, 21.0. IR (cm⁻¹): 3274, 2923, 1771, 1713, 1666, 1623, 1547, 1458, 1351 1218, 1118. HRMS (ESI) m/z calcd for C₂₀H₁₈N₂O₃ [M+Na]^+: 357.1210, found 357.1222.

(E)-4-(1,3-dioxoisindolin-2-yl)-N-(4-methoxybenzyl)but-2-enamide (7c)
Following GP5 with amide 1c (1 equiv, 100 mg, 0.48 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/Cyclohexane 1:1) to afford 7c in 53% (90 mg, 0.26 mmol). White solid, mp: 178-180 °C. 1H NMR (CDCl3, 400 MHz): δ 7.81-7.76 (m, 2H), 7.71-7.65 (m, 2H), 7.16-7.10 (m, 2H), 6.80-6.73 (m, 3H), 5.81 (td, 1H, J = 1.6, 15.3 Hz), 5.61 (br s, 1H), 4.32-4.36 (m, 4H), 3.71 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ 167.6, 164.4, 159.1, 136.8, 134.2, 131.9, 129.9, 125.7, 123.5, 114.1, 55.3, 43.4, 39.2. IR (cm⁻¹) ν: 3284, 2926, 1708, 1620, 1513, 1247. HRMS (ESI) m/z calcld for C20H18N2O4 [M+Na]+: 373.1159, found 373.1163.

(E)-4-(1,3-dioxoisindolin-2-yl)-N-(3-methoxybenzyl)but-2-enamide (7d)

Following GP5 with amide 1d (1 equiv, 100 mg, 0.48 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/Cyclohexane 1:1) to afford 7d in 76% yield (129 mg, 0.37 mmol). White solid, mp: 143-144 °C. 1H NMR (CDCl3, 400 MHz): δ 7.84-7.75 (m, 2H), 7.75-7.62 (m, 2H), 7.18-7.10 (m, 1H), 6.84-6.70 (m, 4H), 5.83 (dt, 1H, J = 15.3, 1.7 Hz), 5.66 (br s, 1H), 4.43-4.31 (m, 4H), 3.72 (d, 3H, J = 5.9 Hz). 13C NMR (CDCl3, 100 MHz): δ 167.6, 164.4, 159.9, 139.4, 136.9, 134.2, 131.9, 129.8, 125.5, 123.5, 120.1, 113.4, 113.1, 55.2, 43.7, 38.2. IR (cm⁻¹) ν: 3275, 2897, 1702, 1631, 1423, 1046, 718. HRMS (ESI) m/z calcld for C20H18N2O4 [M+Na]+: 373.1159, found 373.1157.

(E)-4-(1,3-dioxoisindolin-2-yl)-N-(furan-2-ylmethyl)but-2-enamide (7g)

Following GP5 with amide 1g (1 equiv, 85 mg, 0.51 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/Cyclohexane 1:1) to afford 7g in 20% (30 mg, 0.097 mmol). Pale yellow solid, mp: 144-145 °C. 1H NMR (CDCl3, 400 MHz): δ 7.78 (dd, 2H, J = 3.0, 5.4 Hz), 7.66 (dd, 2H, J = 3.0, 5.4 Hz), 7.25 (dd, 1H, J = 0.9, 1.9 Hz), 6.76 (td, 1H, J = 5.5, 15.3 Hz), 6.22 (dd, 1H, J = 1.9, 3.2 Hz), 6.14 (dd, 1H, J = 0.9, 3.3 Hz), 5.82 (td, 1H, J = 1.6, 15.3 Hz), 5.75 (br s, 1H), 4.39 (d, 2H, J = 5.6 Hz), 4.34 (dd, 2H, J = 1.7, 5.5 Hz). 13C NMR (CDCl3, 100 MHz): δ 167.6, 164.3, 150.8, 142.2, 137.1, 134.2, 131.9, 125.4, 123.5, 110.5, 107.7, 38.2, 36.5. IR (cm⁻¹) ν: 3297, 2917, 1703, 1632, 1556, 1425, 1347, 716. HRMS (ESI) m/z calcld for C17H14N2O4 [M+Na]+: 333.0846, found 333.0857.
(E)-4-(1,3-dioxoisooindolin-2-yl)-N-phenylbut-2-enamide (7h)

Following GP5 with amide 1h (1 equiv, 80 mg, 0.49 mmol) and with 1.5 equiv of phthalimide (109 mg, 0.744 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 7h in 32% yield (44 mg, 0.14 mmol). Pale yellow solid, mp: 173-174 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.93-7.84 (m, 2H), 7.75 (dd, 2H, $J = 5.4, 3.2$ Hz), 7.51 (d, 2H, $J = 7.1$ Hz), 7.31 (t, 2H, $J = 7.9$ Hz), 7.19 (s, 1H), 7.10 (t, 1H, $J = 7.5$ Hz), 6.95 (dt, 1H, $J = 14.7, 5.5$ Hz), 6.05 (d, 1H, $J = 15.0$ Hz), 4.48 (d, 2H, $J = 5.4$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.62, 138.0, 137.6, 134.3, 129.0, 126.1, 124.6, 123.3, 119.9, 38.2. IR (cm$^{-1}$) $\gamma$: 3366, 1769, 1706, 1388, 947, 756. HRMS (ESI) m/z calcd for C$_{18}$H$_{14}$N$_2$O$_3$ [M+Na]$^+$: 329.0897, found 329.0901.

(E)-4-(1,3-dioxoisooindolin-2-yl)-N-phenethylbut-2-enamide (7i)

Following GP5 with amide 1i (1 equiv, 100 mg, 0.53 mmol). The crude product was purified by flash chromatography on silica gel (eluent: AcOEt/CycloHexane 1:1) to afford 7i in 82% yield (145 mg, 0.43 mmol). Pale yellow solid, mp: 148-150 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.78 (dd, 2H, $J = 3.1, 5.4$ Hz), 7.66 (dd, 2H, $J = 3.1, 5.5$ Hz), 7.25-7.09 (m, 5H), 6.71 (td, 1H, $J = 5.6, 15.2$ Hz), 5.76 (td, 1H, $J = 1.6, 15.2$ Hz), 5.41 (br s, 1H), 4.33 (dd, 2H, $J = 1.6, 5.7$ Hz), 3.49 (dt, 2H, $J = 5.9, 6.9$ Hz), 2.75 (t, 2H, $J = 6.9$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.7, 164.6, 138.7, 136.5, 134.2, 131.9, 128.7, 128.6, 126.5, 125.8, 123.5, 40.6, 38.2, 35.5. IR (cm$^{-1}$) $\gamma$: 3284, 2929, 1711, 1391, 717. HRMS (ESI) m/z calcd for C$_{20}$H$_{18}$N$_2$O$_3$ [M+Na]$^+$: 357.1210, found 357.1211.
V-¹H, ¹³C and ¹⁹F NMR Spectra

N-Benzyl-3-butenamide (1a)

Parameter | Value
--- | ---
1 Solvent | CDCl₃
2 Experiment | 1D
3 Number of Scans | 8
4 Spectrometer Frequency | 300.16
5 Nuclei | 14

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[Chemical structure and NMR spectrum image]

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$N$-(4-methylbenzyl)-3-butenamide (1b)
**N-(4-methoxybenzyl)-3-butenamide (1c)**

![Chemical structure of N-(4-methoxybenzyl)-3-butenamide (1c)]
N-(3-methoxybenzyl)-3-butenamide (1d)
$N$-(4-nitrobenzyl)$)-3$-butenamide (1e)
$N$-[(4-(trifluoromethyl)benzyl)but-3-enamide (1f)]
**N-(2-furanylmethyl)-3-butenamide (1g)**

![Chemical structure](image)

**Parameter**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Solvent</td>
<td>CDCl3</td>
</tr>
<tr>
<td>2 Temperature</td>
<td>259.3</td>
</tr>
<tr>
<td>3 Pulse Sequence</td>
<td>zg/300</td>
</tr>
<tr>
<td>4 Spectrometer Frequency</td>
<td>300.16</td>
</tr>
<tr>
<td>5 Nucleus</td>
<td>1H</td>
</tr>
</tbody>
</table>

![NMR spectrum](image)
N-phenyl-3-butenamide (1h)

N-phenethyl-3-butenamide (1i)
$N,N$-dibenzyl-3-butenamide (1j)
N-methoxy-N-methylbut-3-enamide (1k)

N-methoxy-N-methylbut-3-enamide (1k)
Phenyl Allyl Ketone (1I)

Parameter Value
1. Solvent: CDCl3
2. Experiment: 1D
3. Number of Scans: 3548
4. Spectrometer Frequency: 300.16 MHz
5. Nucleus: 1H
Methyl (E)-(4-(benzylamino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2a)
Methyl (E)-(4-((4-methylbenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2b)
Methyl (E)-(4-((4-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2c)
Methyl (E)-(4-((3-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2d)
Methyl (E)-(4-((4-nitrobenzyl)amino)-4-oxobut-2-en-1-yl)tosyl)carbamate (2e)
Methyl (E)-(4-oxo-4-((4-(trifluoromethyl)benzyl)amino)but-2-en-1-yl)(tosyl)carbamate (2f)
Methyl (E)-(4-((furan-2-ylmethyl)amino)-4-oxobut-2-en-1-yl)(tosyl)carbamate (2g)
Methyl (E)-(4-oxo-4-(phenylamino)but-2-en-1-yl)(tosyl)carbamate (2h)
Methyl (E)-(4-oxo-4-(phenethylamino)but-2-en-1-yl)(tosyl)carbamate (2i)
Methyl (E)-(4-oxo-4-phenylbut-2-en-1-yl)(tosyl)carbamate (2l)

Parameter Value
1. Solvent CDCl3
2. Experiment ID
3. Number of Scans 1024
4. Spectrometer Frequency 500.13 MHz
5. Nucleus $^1$H
Methyl (E)-4-((N-(methoxycarbonyl)-4-methylphenyl)sulfonamido)but-2-enoate (2m)
(E)-N-benzyl-4-((N-tosylacetamido)but-2-enamide (3a)

Parameter Value
1. Solvent CDCl3
2. Experiment ID
3. Number of Scans 1024
4. Spectrometer Frequency 400.13
5. Nucleus 1H

Parameter Value
1. Solvent CDCl3
2. Experiment ID
3. Number of Scans 1024
4. Spectrometer Frequency 400.13
5. Nucleus 1H
(E)-N-benzyl-4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)but-2-enamide (4a)
(E)-4-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-N-(4-methylbenzyl)but-2-enamide (4b)
(E)-4-((1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-N-(4-methoxybenzyl)but-2-enamide (4c)
(E)-4-([1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl])-N-(3-methoxybenzyl)but-2-enamide (4d)
(E)-4-[(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)]-N-(4-nitrobenzyl)but-2-enamide (4e)
Methyl (E)-[4-(benzylamino)-4-oxobut-2-en-1-yl](tert-butylsulfinyl)carbamate (5a)
Methyl (E)-{tert-butylsulfinyl}(4-((4-methylbenzyl)amino)-4-oxobut-2-en-1-yl)carbamate (5b)
Methyl (E)-(tert-butylsulfinyl)(4-((4-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)carbamate (5c)
Methyl (E)-(tert-butylsulfinyl)(4-((3-methoxybenzyl)amino)-4-oxobut-2-en-1-yl)carbamate (5d)
(E)-4-((4-Methylbenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6b)

Parameter Value
1 Solvent D2O
2 Temperature 300.0
3 Spectrometer Frequency 400.12
4 Nucleus 1H

Parameter Value
1 Solvent D2O
2 Experiment ID
3 Number of Scans 32
4 Spectrometer Frequency 400.12
5 Nucleus 1H
(E)-4-((4-Methoxybenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6c)
(E)-4-(((3-methoxybenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6d)
(E)-4-((4-nitrobenzyl)amino)-4-oxobut-2-en-1-yl pivalate (6e)
\((E)-4\text{-oxo-4-}((4\text{-}((\text{trifluoromethyl})\text{benzyl})\text{amino})\text{but-2-en-1-yl pivalate}}\ (6f)\)
(E)-4-((Furan-2-ylmethyl)amino)-4-oxobut-2-en-1-yl pivalate (6g)
(E)-4-Oxo-4-(phenylamino)but-2-en-1-yl pivalate (6h)
(E)-4-Oxo-4-(phenethylamino)but-2-en-1-yl pivalate (6i)
(E)-4-(Dibenzylamino)-4-oxobut-2-en-1-yl pivalate (6j)
(E)-4-(methoxy(methyl)amino)-4-oxobut-2-en-1-yl pivalate (6k)
Methyl (E)-4-(pivaloyloxy)but-2-enoate (6m)
(E)-N-benzyl-4-(1,3-dioxoisooindolin-2-yl)but-2-enamide (7a)
(E)-4-(1,3-dioxoisindolin-2-yl)-N-(4-methylbenzyl)but-2-enamide (7b)
(E)-4-(1,3-dioxoisindolin-2-yl)-N-(4-methoxybenzyl)but-2-enamide (7c)
(E)-4-(1,3-dioxoisindolin-2-yl)-N-(3-methoxybenzyl)but-2-enamide (7d)
(E)-4-(1,3-dioxoisouindolin-2-yl)-N-(furan-2-ylmethyl)but-2-enamide (7g)
(E)-4-(1,3-dioxoisindolin-2-yl)-N-phenylbut-2-enamide (7h)
(E)-4-(1,3-dioxoisindolin-2-yl)-N-phenethylbut-2-enamide (7i)