Supporting Information
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Arylation of Amide and Urea C(sp3)–H Bonds with Aryl Tosylates Generated In Situ from Phenols

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1 General Considerations

All reactions were set up with glovebox and carried out under nitrogen atmosphere in Schlenk tubes. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Anhydrous solvents were purchased from Acros Organics and used as received. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI and used as received unless otherwise stated.

$^1$H and $^{13}$C NMR spectra were recorded on a Brüker Advance 400 spectrometer ($^1$H: 400 MHz, $^{13}$C: 101 MHz). Chemical shifts ($\delta$) for $^1$H and $^{13}$C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra and the chemical shifts converted to the TMS scale (CDCl$_3$: $\delta$H = 7.26 ppm, $\delta$C = 77.16 ppm; CD$_3$OD: $\delta$H = 3.31 ppm, $\delta$C = 49.00 ppm; (CD$_3$)$_2$SO: $\delta$H = 2.50 ppm, $\delta$C = 39.52 ppm).

GC-MS was obtained using electron ionization (SHIMADZU GCMS-QP 2010 SE). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Exact ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. ESI-MS were obtained on a Thermo LTQ mass spectrometer.
Synthesis and Characterization of Products.

General procedure for the synthesis of 3

To a flame-dried 10 mL Schlenk tube A equipped with a magnetic stir bar was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)(PF$_6$) (0.012 mmol). The tube was triple evacuated/N$_2$ filled before being transferred into a glovebox. NiBr$_2$·glyme (0.015 mmol), Me$_4$Phen (0.015 mmol) and Li$_2$CO$_3$ (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. 1a (1.0 mL) were added to the tube, followed by 3-acetoxyquinuclidine (0.33 mmol), 2a (0.3 mmol), TsCl (0.45 mmol), Cs$_2$CO$_3$ (0.6 mmol) and 1a (5.0 mL) were combined in a 10-mL Schlenk tube B, after stirring at r.t. for 30 mins, it was filtered through an acrodisc into Schlenk tube A using a syringe. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 36 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 5:1 to 1:1) to provide the pure product 3aa as a pale yellow oil in 85% yield (64.6 mg, 0.255 mmol).

Tips:
1) Get rid of heat with fans.
2) Avoid other light source irradiation.
Procedure for the synthesis of 3gb

To a flame-dried 10 mL Schlenk tube A equipped with a magnetic stir bar was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)(PF$_6$) (0.012 mmol). The tube was triple evacuated/N$_2$ filled before being transferred into a glovebox. NiBr$_2$:glyme (0.015 mmol), Me$_4$Phen (0.015 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. 1g (0.9 mmol) were added to the tube, followed by 3-acetoxyquinuclidine (0.33 mmol). 2b (0.3 mmol), TsCl (0.45 mmol), Cs$_2$CO$_3$ (0.6 mmol) and DMF (3.0 mL) were combined in a 10-mL Schlenk tube B, after stirring at r.t. for 30 mins, it was filtered through an acrodisc into Schlenk tube A using a syringe. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 36 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 5:1 to 1:1) to provide the pure product 3gb as a colorless oil in 42% yield (36.3 mg, 0.125 mmol).

$N$-(4-benzoylbenzyl)$-N$-methylformamide (3aa)

\[
\begin{align*}
& \text{O} \\
& \text{N} \\
& \text{COPh} \\
& \text{Ph}
\end{align*}
\]

64.6 mg, 0.255 mmol, 85%;

Pale yellow oil;

R$_f$(PE:EA=1:1): 0.2;

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.27 (d, J = 46.8 Hz, 1H), 7.87 – 7.76 (m, 4H), 7.65 – 7.55 (m, 1H), 7.49 (ddd, J = 8.5, 6.7, 3.9 Hz, 2H), 7.39 – 7.30 (m, 2H), 4.56 (d, J = 42.1 Hz, 2H), 2.88 (d, J = 35.8 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.22, 195.03, 161.78, 161.68, 139.71, 139.44, 136.39, 136.25, 135.92, 131.62, 131.50, 129.65, 129.50, 128.97, 127.34, 127.29, 126.89, 126.18, 52.13, 46.54, 33.25, 28.65.

Exact Mass ESI-MS: calculated m/z for [C$_{16}$H$_{15}$NO$_2$+H]$^+$: 254.1176, found: 254.1176.
N-(4-benzoylbenzyl)-N-methylacetamide (3ba)

\[
\text{O} \quad \text{N} \quad \text{COPh} \\
\text{O} \quad \text{N} \quad \text{COPh}
\]

43.2 mg, 0.162 mmol, 54%;
Pale yellow oil;
\[R_f\text{(PE:EA}=20:1\text{)}: 0.2;\]
\[\text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.79 (dddd, \text{ } J = 11.7, 8.1, 6.4, 1.9 \text{ Hz, } 4\text{H}), 7.64 – 7.55 \text{ (m, } 1\text{H}), 7.49 (\text{td, } J = 7.5, 5.8 \text{ Hz, } 2\text{H}), 7.39 – 7.27 \text{ (m, } 2\text{H}), 4.65 (\text{d, } J = 19.2 \text{ Hz, } 2\text{H}), 2.98 (\text{s, } 3\text{H}), 2.18 (\text{d, } J = 10.9 \text{ Hz, } 3\text{H}).\]
\[\text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 195.27, 195.03, 169.99, 169.88, 141.15, 140.32, 136.47, 136.30, 135.97, 135.59, 131.56, 131.42, 129.73, 129.42, 128.95, 128.93, 127.32, 127.25, 126.63, 125.10, 53.02, 49.46, 34.84, 32.89, 20.76, 20.44.\]
Exact Mass ESI-MS: calculated m/z for \([\text{C}\text{17H}_{17}\text{NO}_2+\text{H}]^+\): 268.1332, found: 268.1332.

N-(1-(4-benzoylphenyl)ethyl)-N-ethylacetamide (3ca)

\[
\text{O} \quad \text{N} \quad \text{COPh} \\
\text{O} \quad \text{N} \quad \text{COPh}
\]

79.4 mg, 0.269 mmol, 90%;
Pale yellow oil;
\[R_f\text{(PE:EA}=1:1\text{)}: 0.1;\]
\[\text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.71 (\text{td, } J = 8.0, 6.4 \text{ Hz, } 3\text{H}), 7.51 (\text{td, } J = 6.3, 5.1, 2.2 \text{ Hz, } 1\text{H}), 7.45 – 7.27 \text{ (m, } 4\text{H}), 5.52 (\text{q, } J = 7.1 \text{ Hz, } 1\text{H}), 3.54 – 2.70 \text{ (m, } 2\text{H}), 2.12 (\text{s, } 3\text{H}), 1.56 (\text{d, } J = 7.1 \text{ Hz, } 3\text{H}), 0.97 (\text{t, } J = 7.1 \text{ Hz, } 3\text{H}).\]
\[\text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 195.26, 169.68, 145.18, 136.49, 135.43, 131.42, 129.19, 128.96, 127.26, 126.26, 49.72, 38.16, 20.80, 15.91, 15.13.\]
Exact Mass ESI-MS: calculated m/z for \([\text{C}\text{19H}_{21}\text{NO}_2+\text{H}]^+\): 296.1645, found: 296.1639.

1-(4-benzoylbenzyl)-3-methylimidazolidin-2-one (3da)

\[
3\text{da} \quad 3\text{da}' \quad 2:1
\]

57.2 mg, 0.194 mmol, 65%;
Pale yellow oil;
\[R_f\text{(PE:EA}=3:1\text{)}: 0.2;\]
\[ ^1H\text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.89 - 7.73 \ (m, 4H), 7.66 - 7.56 \ (m, 1H), 7.49 \ (qd, J = 6.7, 1.7 \text{ Hz}, 2H), 7.41 \ (dd, J = 18.9, 8.2 \text{ Hz}, 2H), 4.54 - 4.42 \ (m, 1H), 3.43 - 3.16 \ (m, 2H), 2.86 \ (s, 3H), 2.69 \ (s, 3H). \]

\[ ^{13}C\text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 195.08, 160.68, 143.20, 136.66, 136.30, 131.59, 129.74, 128.98, 127.33, 125.80, 59.23, 52.89, 30.28, 28.89. \]

**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{18}\text{H}_{18}\text{N}_{2}\text{O}_{2}+\text{H}]^+\): 295.1441, found: 295.1441.

1-(4-benzoylbenzyl)-1,3,3-trimethylurea (3ea)

57.6 mg, 0.194 mmol, 65%;
Pale yellow oil;
\[ R_f (\text{PE:EA}=1:1): 0.1; \]

\[ ^1H\text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.76 - 7.65 \ (m, 4H), 7.54 - 7.47 \ (m, 1H), 7.44 - 7.36 \ (m, 2H), 7.35 - 7.29 \ (m, 2H), 4.38 \ (s, 2H), 2.79 \ (s, 6H), 2.71 \ (s, 3H). \]

\[ ^{13}C\text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 195.32, 164.38, 142.13, 136.56, 135.44, 131.37, 129.42, 128.96, 127.24, 126.40, 52.88, 37.70, 35.95. \]

**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{18}\text{H}_{20}\text{N}_{2}\text{O}_{2}+\text{H}]^+\): 297.1598, found: 297.1592.

5-(4-benzoylphenyl)-1-methylpyrrolidin-2-one (3fa)

79.0 mg, 0.283 mmol, 94%;
Pale yellow oil;
\[ R_f (\text{PE:EA}=1:1): 0.2; \]

**Major regioisomer 5et:**

\[ ^1H\text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.80 - 7.71 \ (m, 4H), 7.58 - 7.51 \ (m, 1H), 7.47 - 7.40 \ (m, 2H), 7.25 \ (d, J = 8.3 \text{ Hz}, 2H), 4.55 \ (dd, J = 8.2, 5.5 \text{ Hz}, 1H), 2.65 \ (s, 3H), 2.58 - 2.34 \ (m, 3H), 1.90 - 1.76 \ (m, 1H). \]

\[ ^{13}C\text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 195.02, 174.55, 144.80, 136.39, 136.29, 131.58, \]
129.86, 128.96, 127.33, 125.20, 63.27, 28.96, 27.38, 27.28.

**Exact Mass ESI-MS:** calculated m/z for \([C_{18}H_{17}NO_2+H]^+\): 280.1332, found: 280.1320.

**tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (3gb)**

![Chemical structure of tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (3gb)]

36.3 mg, 0.125 mmol, 42%; Colorless oil;

\[ R_f (PE:EA = 5:1) : 0.3; \]

**\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\):** 8.06 – 7.77 (m, 2H), 7.41 – 7.01 (m, 2H), 5.08 – 4.71 (m, 1H), 3.65 (t, \(J = 6.8\) Hz, 2H), 2.59 (d, \(J = 8.6\) Hz, 3H), 2.36 (dt, \(J = 14.2, 7.9\) Hz, 1H), 2.00 – 1.72 (m, 3H), 1.46 (s, 3H), 1.18 (s, 6H).

**\(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\):** 197.81, 154.43, 150.81, 135.72, 128.64, 128.44, 125.64, 79.54, 61.17, 60.67, 47.40, 47.15, 35.90, 34.75, 28.49, 28.16, 26.62, 23.66, 23.26.

**GCMS:** calculated m/z for \(C_{17}H_{23}NO_3\): 289.2, found: 289.2.

**5-(4-acetylphenyl)-1-methylpyrrolidin-2-one (3fb)**

![Chemical structures of 5-(4-acetylphenyl)-1-methylpyrrolidin-2-one (3fb) and its regioisomer (3fb')] 7:1

46.6 mg, 0.214 mmol, 72%; Pale yellow oil;

\[ R_f (PE:EA=1:1) : 0.2; \]

**Major regioisomer 5ej:** **\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\):** 7.99 (d, \(J = 8.4\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 4.79 – 4.50 (m, 1H), 2.70 (s, 3H), 2.62 (s, 3H), 2.57 – 2.43 (m, 2H), 1.95 – 1.77 (m, 1H).

**\(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\):** 196.47, 174.54, 145.50, 135.90, 128.15, 125.50, 63.20, 28.94, 27.33, 27.21, 25.67.

**Exact Mass ESI-MS:** calculated m/z for \([C_{13}H_{15}NO_2+H]^+\): 218.1176, found: 218.1164.
5-(3-acetylphenyl)-1-methylpyrrolidin-2-one (3fc)

42.0 mg, 0.192 mmol, 64%;
Pale yellow oil;
R_f(PE:EA=1:1): 0.2;

Major regioisomer 5ep

^{1}H NMR (400 MHz, CDCl₃) δ 7.92 (dt, J = 7.7, 1.5 Hz, 1H), 7.82 (t, J = 1.9 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.42 (dt, J = 7.7, 1.5 Hz, 1H), 4.67 – 4.55 (m, 1H), 2.68 (s, 3H), 2.63 (s, 3H), 2.59 – 2.43 (m, 3H), 1.96 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, CDCl₃) δ 196.70, 174.57, 140.90, 136.82, 129.75, 128.46, 127.27, 125.20, 63.37, 29.08, 27.41, 27.30, 25.72.

Exact Mass ESI-MS: calculated m/z for [C₁₄H₁₄NO₂H]⁺: 218.1176, found:218.1166.

5-(7-methoxynaphthalen-2-yI)-1-methylpyrrolidin-2-one (3fd)

51.3 mg, 0.201 mmol, 67%;
Pale yellow oil;
R_f(PE:EA=1:1): 0.2;

Major regioisomer 5eb

^{1}H NMR (400 MHz, CDCl₃) δ 7.75 (m, 2H), 7.58 (d, J = 1.8 Hz, 1H), 7.26 (dd, J = 8.5, 1.9 Hz, 1H), 7.21 – 7.10 (m, 2H), 4.72 – 4.59 (m, 1H), 3.92 (s, 3H), 2.70 (d, J = 0.8 Hz, 3H), 2.56 – 2.38 (m, 3H), 2.07 – 1.81 (m, 2H).

Exact Mass ESI-MS: calculated m/z for [C₁₆H₁₇NO₂H]⁺: 256.1332, found: 256.1326.
5-((1,1'-biphenyl)-4-yl)-1-methylpyrrolidin-2-one (3fe)

57.0 mg, 0.228 mmol, 76%;
Pale yellow oil;

\[ \text{Rf (PE:EA=3:1): 0.2} \]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 – 7.48 (m, 4H), 7.39 – 7.32 (m, 2H), 7.30 – 7.23 (m, 1H), 7.21 – 7.12 (m, 2H), 4.47 (dd, \(J = 7.6, 5.8\) Hz, 1H), 2.62 (s, 3H), 2.58 – 2.26 (m, 3H), 1.89 – 1.76 (m, 1H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 174.52, 140.02, 139.39, 139.07, 127.80, 126.70, 126.46, 126.00, 125.78, 63.30, 29.15, 27.44, 27.26.

\text{Exact Mass ESI-MS: calculated m/z for [C}_{17}\text{H}_{17}\text{NO}^+\): 252.1383 found: 252.1371.

1-methyl-5-((4-oxo-2-phenyl-4H-chromen-7-yl)pyrrolidin-2-one (3ff)

57.2 mg, 0.179 mmol, 60%;
Pale yellow solid;

\[ \text{Rf (PE:EA=1:5): 0.2} \]

\text{Major regioisomer 5ej: } ^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.17 (d, \(J = 8.2\) Hz, 1H), 7.90 – 7.82 (m, 2H), 7.53 – 7.44 (m, 3H), 7.34 (d, \(J = 1.6\) Hz, 1H), 7.24 – 7.17 (m, 1H), 6.76 (s, 1H), 4.62 (dd, \(J = 7.7, 5.3\) Hz, 1H), 2.70 (s, 3H), 2.57 – 2.32 (m, 2H), 1.93 – 1.79 (m, 1H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 176.88, 174.53, 162.50, 155.62, 147.01, 130.76, 130.45, 128.09, 125.86, 125.26, 122.27, 114.42, 106.65, 63.11, 28.74, 27.50, 27.14.

\text{Exact Mass ESI-MS: calculated m/z for [C}_{20}\text{H}_{17}\text{NO}_3^+\): 320.1281, found: 320.1267.
1-methyl-5-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydرو-6H-cyclopenta[a]phenanthren-3-yl)pyrrolidin-2-one (3fg)

54.6 mg, 0.155 mmol, 52%;
Pale yellow solid;
R_f (PE:EA=1:2): 0.2;

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.25 (m, 1H), 6.98 (dd, J = 8.1, 2.0 Hz, 1H), 6.92 (d, J = 1.9 Hz, 1H), 4.47 (dd, J = 7.4, 5.5 Hz, 1H), 2.92 (dd, J = 9.5, 4.3 Hz, 2H), 2.68 (d, J = 2.0 Hz, 3H), 2.62 – 1.37 (m, 20H), 0.92 (s, 3H).

^13C NMR (101 MHz, CDCl_3) δ 220.79, 175.59, 139.66, 138.53, 137.24, 126.78, 126.02, 123.75, 64.34, 50.48, 47.96, 44.37, 38.06, 35.85, 31.57, 30.21, 29.48, 29.45, 28.47, 28.31, 28.30, 26.44, 26.43, 25.70, 25.68, 21.59, 13.86.

Exact Mass ESI-MS: calculated m/z for [C_{23}H_{29}NO_2+H]^+: 352.2271, found: 352.2271.
3 Copies of NMR spectra

$N$-(4-benzoylbenzyl)-$N$-methylformamide (3aa)
N-(4-benzoylbenzyl)-N-methylacetamide (3ba)
$N$-(1-(4-benzoylephynyl)ethyl)-$N$-ethylacetamide (3ca)
1-(4-benzoylbenzyl)-3-methylimidazolidin-2-one (3da)
1-(4-benzoylbenzyl)-1,3,3-trimethylurea (3da)
5-(4-benzoylphenyl)-1-methylpyrrolidin-2-one (3fa)
tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (3gb)
5-(4-acetylphenyl)-1-methylpyrrolidin-2-one (3fb)
5-(3-acetylphenyl)-1-methylpyrrolidin-2-one (3fc)
5-(7-methoxynaphthalen-2-yl)-1-methylpyrrolidin-2-one (3fd)
5-([1,1'-biphenyl]-4-yl)-1-methylpyrrolidin-2-one (3fe)
1-methyl-5-(4-oxo-2-phenyl-4H-chromen-7-yl)pyrrolidin-2-one (3ff)
1-methyl-5-((8R,9S,13S,14S)-13-methyl-17-oxo-7,9,11,12,13,14,15,16,17-decahydron-6H-cyclopenta[a]phenanthren-3-yl)pyrrolidin-2-one (3fg)