Electronic Supplementary Information

Ni-Catalyzed Cross-Coupling Reactions of N-Acylpyrrole-Type Amides

with Organoboron Reagents

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General information

Unless otherwise stated, reactions were run under an Argon atmosphere with rigid exclusion of moisture from reagents and glassware. All glassware was dried in Infrared rapid drying box prior to use. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker 400 or Bruker 500 ($^1$H/400 or 500 MHz, $^{13}$C/100 or 125 MHz) spectrometer. Chemical shifts are expressed in parts per million (δ) relative to an internal standard of tetramethylsilane (TMS). ESI-Mass spectra were recorded on a Bruker Dalton ESquire 3000 plus MS apparatus. Optical rotations were measured with an Anton Paar MCP 500 polarimeter. Melting points were uncorrected. Infrared spectra were recorded with a Nicolet Avatar 330 FT-IR spectrometer using film KBr pellet technique. HRMS spectra were recorded on a Bruker En Apex ultra 7.0T FT-MS apparatus.

Experimental procedures and characterization data

1. Reaction optimization and Control experiments

Table S1. Optimization of the catalyst and ligand."
<p>| | | | |</p>
<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Ni(COD)$_2$ (10)</td>
<td></td>
<td>PCy$_3$ (10)</td>
</tr>
<tr>
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<td>Ni(COD)$_2$ (10)</td>
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<td>PPh$_3$ (10)</td>
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<td>Ni(COD)$_2$ (10)</td>
<td></td>
<td>2,2-bipyridine (10)</td>
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<td>9</td>
<td>Ni(COD)$_2$ (10)</td>
<td></td>
<td>L1-HCl/t-BuOK (10)</td>
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<td>Ni(COD)$_2$ (10)</td>
<td>L1-HCl (10)</td>
<td>33</td>
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<td>L2-HCl (10)</td>
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<td>12</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L3-HCl (10)</td>
<td>45 (41$^a$)</td>
</tr>
<tr>
<td>13</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L4-HCl (10)</td>
<td>13 (9$^a$)</td>
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<tr>
<td>14</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L5-HBF$_4$ (10)</td>
<td>38</td>
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<tr>
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<td>Ni(COD)$_2$ (10)</td>
<td>L6-2HCl (10)</td>
<td>51 (49$^a$)</td>
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<tr>
<td>16</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L9-4HBr (10)</td>
<td>86 (83$^a$)</td>
</tr>
<tr>
<td>17</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L7-2HCl (10)</td>
<td>88 (86$^a$)</td>
</tr>
<tr>
<td>18</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L8-2HCl (10)</td>
<td>96 (94$^a$)</td>
</tr>
<tr>
<td>19</td>
<td>Ni(COD)$_2$ (10)</td>
<td>L8-2HCl (5)</td>
<td>57</td>
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<tr>
<td>20</td>
<td>Ni(COD)$_2$ (10)</td>
<td>IPr-HCl/t-BuOK (20)</td>
<td>89 (87 $^a$)</td>
</tr>
<tr>
<td>21</td>
<td>Ni(COD)$_2$ (10)</td>
<td>IMes-HCl/t-BuOK (10)</td>
<td>Trace</td>
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$^a$ Yields were determined by $^1$H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as a internal standard. $^a$ Isolated yields.

A vial packaged with tin foil was charged with powdered K$_3$PO$_4$ (101.9 mg, 0.48 mmol, 2.0 equiv), N-acylpyrrole 1a (41.1 mg, 0.24 mmol, 1.0 equiv), arylboronic acid neopentyl glycol
ester 2a (105.6 mg, 0.48 mmol, 2.0 equiv), ligand (y mol%) and a magnetic stir bar. Then the vial was taken into a glove box and charged with cat. (x mol%). After that, toluene (0.48 mL, 0.5 M) and water (8.6 µL, 0.48 mmol, 2.0 equiv) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (1 mL), washed with a saturated aqueous Na₂CO₃ solution (1 mL) and brine (1 mL), and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was analyzed by ¹H NMR or purified by flash column chromatography to yield the desired ketone 3aa.

**Table S2. Optimization of the base, solvent and additive.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>base</th>
<th>solvent</th>
<th>additive (x equiv)</th>
<th>Yield° of 3aa (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Et₃N</td>
<td>Toluene</td>
<td>H₂O (2)</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Ba(OH)₂</td>
<td>Toluene</td>
<td>H₂O (2)</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>LiCl</td>
<td>Toluene</td>
<td>H₂O (2)</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>Cs₂CO₃</td>
<td>Toluene</td>
<td>H₂O (2)</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>K₂CO₃</td>
<td>Toluene</td>
<td>H₂O (2)</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>K₃PO₄</td>
<td>Toluene</td>
<td>H₂O (2)</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>K₃PO₄</td>
<td>Toluene</td>
<td>H₂O (4)</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>K₃PO₄</td>
<td>Toluene</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>9</td>
<td>K₃PO₄</td>
<td>THF</td>
<td>H₂O (2)</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>K₃PO₄</td>
<td>DMF</td>
<td>H₂O (2)</td>
<td>4</td>
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<tr>
<td>11</td>
<td>K₃PO₄</td>
<td>1,4-dioxane</td>
<td>H₂O (2)</td>
<td>Trace</td>
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<tr>
<td>12</td>
<td>K₃PO₄</td>
<td>Toluene</td>
<td>H₂BO₃ (2)</td>
<td>0</td>
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<tr>
<td>13</td>
<td>K₃PO₄</td>
<td>Toluene</td>
<td>TMSOTf (2)</td>
<td>10</td>
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<tr>
<td>14</td>
<td>K₃PO₄</td>
<td>Toluene</td>
<td>4Å MS (2)</td>
<td>30</td>
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</table>

° Yields were determined by ¹H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. Nep = neopentylglycol.

A vial packaged with tin foil was charged with base (0.48 mmol, equiv), N-acylpyrrole 1a (41.1 mg, 0.24 mmol, 1.0 equiv), arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol, 2.0 equiv), L8·2HCl (16.2 mg, 0.024 mmol, 10 mol%) and a magnetic stir bar. Then the vial was taken into a glove box and charged with Ni(COD)₂ (6.6 mg, 0.024 mmol, 10 mol %). After that, solvent (0.48 mL, 0.5 M) and additive was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (1 mL), washed with a saturated aqueous Na₂CO₃ solution (1mL) and brine (1 mL), and then dried over anhydrous Na₂SO₄. The combined organic layer was filtered and concentrated under reduced pressure. The residue
was analyzed by $^1$H NMR or purified by flash column chromatography to yield the desired ketone 3aa.

**Table S3.** Optimisation of the Temp, concentration.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp (°C)</th>
<th>concentration [n M]</th>
<th>Yield$^a$ of 3aa</th>
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<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>0.50</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>0.50</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>RT</td>
<td>0.50</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>0.50</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>0.25</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>1.00</td>
<td>65</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. RT = room temperature. Temp = temperature.

A vial packaged with tin foil was charged with powdered K$_3$PO$_4$ (101.9 mg, 0.48 mmol, 2.0 equiv), N-acylpyrrole 1a (41.1 mg, 0.24 mmol, 1.0 equiv), arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol, 2.0 equiv), L8·2HCl (16.2 mg, 0.024 mmol, 10 mol%) and a magnetic stir bar. Then the vial was taken into a glove box and charged with Ni(COD)$_2$ (6.6 mg, 0.024 mmol, 10 mol%) and water (8.6 uL, 0.48 mmol, 2.0 equiv) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at x °C for 20 h. After cooling to room temperature, the mixture was diluted with CH$_2$Cl$_2$ (1 mL), washed with a saturated aqueous Na$_2$CO$_3$ solution (1 mL) and brine (1 mL), and then dried over anhydrous Na$_2$SO$_4$. The combined organic layer was filtered and concentrated under reduced pressure. The residue was analyzed by $^1$H NMR or purified by flash column chromatography to yield the desired ketone 3aa.

**Table S4.** Screening different organoboron compounds in the cross-coupling reactions of N-acylpyrrole 1a.
Yields were determined by $^1$H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. * Isolated yields.

Table S5. Control experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield$^a$ of 3aa (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>L8·2HCl (10 mol%), K$_3$PO$_4$ (2.0 equiv), H$_2$O (2.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Toluene (0.5 M), 60 °C, 20 h</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ni(cod)$_2$ (10 mol%), K$_3$PO$_4$ (2.0 equiv), H$_2$O (2.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Toluene (0.5 M), 60 °C, 20 h</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ni(cod)$_2$ (10 mol%), L8·2HCl (10 mol%), H$_2$O (2.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Toluene (0.5 M), 60 °C, 20 h</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ni(cod)$_2$ (10 mol%), L8·2HCl (10 mol%), K$_3$PO$_4$ (2.0 equiv)</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Toluene (0.5 M), 60 °C, 20 h</td>
<td></td>
</tr>
</tbody>
</table>

*Yields were determined by $^1$H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard.

2. Synthesis of the precursors of NHC Ligands (L2·HCl, L6–L8·2HCl, L9·4HBr)

(1) Synthesis of the precursor of NHC Ligand L2·HCl.
2-(2,6-Diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (L2-HCl)

A reported procedure was followed.\(^4\)

(a) A mixture containing 2,6-diisopropylaniline (3.8 mL, 20.0 mmol), picolinaldehyde (1.9 mL, 20.0 mmol) and EtOH (40.0 mL) was stirred at room temperature for 12 h. Then the reaction mixture was filtered, and the precipitate was washed with cold EtOH (10 mL), after dried in vacuum, gave the desired crude imine.

(b) Chloromethyl ethyl ether (2.1 mL, 22 mmol) was added dropwise to the solution of imine (prepared above) in THF (50.0 mL) under Argon. The reaction was stirred at 40 °C for 18 h. Then the mixture was dried under vacuum. The residue was purified by flash column chromatography (eluent: MeOH/CH\(_2\)Cl\(_2\) = 1/5) and recrystallization from ethyl acetate to afforded desired product L2-HCl as a white solid (3.21 g, 51% Yield, over two steps). R\(_f\): 0.4 (MeOH/CH\(_2\)Cl\(_2\) = 1/3); mp: 218-220 °C; IR (film): 3054, 2962, 2920, 1651, 1601, 1542, 1467, 1385, 1365, 1325, 1093, 817, 761; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 11.3 (s, 1H), 9.83 (s, \(J = 7.0\) Hz, 1H), 7.80 (d, \(J = 9.5\) Hz, 1H), 7.64 (s, 1H), 7.59 (t, \(J = 7.8\) Hz, 1H), 7.38-7.30 (m, 3H), 7.13 (t, \(J = 6.8\) Hz, 1H), 2.13 (sept, \(J = 6.8\) Hz, 2H), 1.23 (d, \(J = 6.8\) Hz, 6H), 1.15 (d, \(J = 6.8\) Hz, 6H); \(^13\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 145.1 (2C), 132.0, 130.6, 130.1, 129.3, 126.3, 126.5, 126.3, 124.6 (2C), 117.7, 117.4, 113.8, 28.7 (2C), 24.44 (2C), 24.37 (2C); HRMS (ESI) m/z calcd for [C\(_{19}\)H\(_{23}\)N\(_2\)]\(^+\) (M-Cl\(^-\)): 279.1856; found: 279.1865.

(2) Synthesis of the precursors of NHC Ligands L6–L8•2HCl, L9•4HBr.
General procedure A for synthesis of the precursors of NHC Ligands L6–L8·2HCl, L9·4HBr from aromatic amines.

A reported procedure with some modifications was followed.

(a) A solution of aromatic amines (50.0 mmol, 1.0 equiv) in MeOH (100.0 mL, 0.5 M) was added glyoxal (40% aq, 5.5 mL, 50.0 mmol, 1.0 equiv) at 0 °C and the reaction was stirred for 16 h at RT. Then NH₄Cl (5.35 g, 100.0 mmol, 2.0 equiv) was added followed by formaldehyde (37% aq, 7.5 mL, 100.0 mmol, 2.0 equiv). The mixture was diluted with MeOH (200 mL, 0.25 M) and the resulting mixture was refluxed for 1 h. After that, H₃PO₄ (85%, 4.6 mL, 75.0 mmol, 1.5 equiv) was added over a period of 10 mins. The resulting mixture was then reflux for a further 5 h. The reaction was monitored by TLC. After removal of the solvent, the dark residue was poured into ice and neutralized with aq 40% KOH solution until pH 9. The resulting mixture was extracted with Et₂O (5×70 mL). The combined organic layer was washed with H₂O (60 mL) and brine (60 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) affording the desired 1-arylimidazole 13.

(b) A mixture containing 1-arylimidazole 13 (20.0 mmol, 1.0 equiv), 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol, 0.5 equiv) or 1,2,4,5-tetrakis(bromomethyl)benzene (2.25 g, 5.0 mmol, 0.25 equiv) and o-xylene (100.0 mL, 0.2 M) was refluxed for 24 h. The reaction was monitored by TLC. After removal of the solvent, the residue was purified by flash column chromatography to afford crude product. Then the crude product was recrystallization from ethyl acetate to afford the desired precursor of NHC ligand.

1,1’-((2,4,6-Trimethyl-1,3-phenylene)bis(methylene))bis(3-mesityl-1H-imidazol-3-ium) chloride (L6·2HCl)
Following general procedure A-(a), the reaction of 2,4,6-trimethylaniline (7.02 mL, 50.0 mmol) with glyoxal (40% aq, 5.5 mL, 50.0 mmol), NH₄Cl (5.35 g, 100.0 mmol) and formaldehyde (37% aq, 7.5 mL, 100.0 mmol), afforded 1-arylimidazole 13a as a yellow solid (4.10 g, 44% Yield), Rf: 0.3 (EtOAc/Hexane = 1/5). The spectral data were identical with those reported in the literature.⁵

Following general procedure A-(b), the reaction of 1-Arylimidazole 13a (3.73 g, 20.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded L6·2HCl as a light yellow solid (4.36 g, 74% Yield). Rf: 0.4 (MeOH/CH₂Cl₂ = 1/3); mp: the compound decomposed at 275 °C; IR (film): 2969, 1653, 1635, 1607, 1544, 1486, 1456, 1384, 1266, 1195, 1180, 1156, 1142, 1075, 1036, 969, 855, 730 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 10.63 (s, 2H), 8.08 (s, 2H), 7.18 (t, J = 1.73 Hz, 2H), 7.00 (br s, 2H), 6.99 (s, 2H), 6.95 (s, 1H), 6.07 (s, 4H), 2.47 (s, 3H), 2.34 (s, 6H), 2.33 (s, 6H), 2.06 (s, 6H), 2.05 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 141.1 (2C), 140.1 (2C), 138.9, 137.7 (2C), 134.1 (4C), 131.8 (2C), 130.8 (2C), 129. 8 (4C), 128.3, 123.8 (2C), 123.6 (2C), 48.4 (2C), 21.1 (2C), 20.1 (2C), 17.6 (4C), 16.7; HRMS (ESI) m/z calcld for [C₃₅H₂₆ClN₄]⁺ (M+Cl⁺): 553.3093; found: 553.3096.

1,1'-(2,4,6-Trimethyl-1,3-phenylene)bis(methylenecarbonyl)bis(3-(2,4,6-triisopropylphenyl)-1H-imidazol-3-ium) chloride (L8·2HCl)

Following general procedure A-(a), the reaction of 2,4,6-triisopropylaniline (10.97 g, 50.0 mmol) with glyoxal (40% aq, 5.5 mL, 50.0 mmol), NH₄Cl (5.35 g, 100.0 mmol) and formaldehyde (37% aq, 7.5 mL, 100.0 mmol), afforded 1-Arylimidazole 13b as a light yellow solid (6.76 g, 50% Yield). Rf: 0.3 (EtOAc/Hexane = 1/5); mp: 186-188 °C; IR (film): 3112, 3095, 2919, 2850, 1643, 1608, 1499, 1470, 1313, 1298, 1281, 1238, 1096, 1066, 909, 776 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.45 (s, 1H), 7.22 (s, 1H), 7.08 (s, 2H), 6.93 (s, 1H), 2.95 (sept, J = 6.9 Hz, 1H), 2.39 (sept, J = 6.9 Hz, 2H), 1.29 (d, J = 6.9 Hz, 6 H), 1.13 (d, J = 6.9 Hz, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 150.4, 146.2 (2C), 138.7, 130.7, 129.3, 121.7 (3C), 34.4, 28.2 (2C), 24.5 (2C), 24.4 (2C), 24.1 (2C); HRMS (ESI) m/z calcld for [C₁₅H₂₀N₄]⁺ (M+H⁺): 271.2169; found: 271.2177.

Following general procedure A-(b), the reaction of 1-Arylimidazole 13b (5.41 g, 20.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded L8·2HCl as a white solid (5.38 g, 71% Yield). Rf: 0.4 (MeOH/CH₂Cl₂ = 1/3); mp: 115-117 °C; IR (film): 2963, 2928, 2870, 1603, 1543, 1462, 1385, 1366, 1265, 1196, 1179, 1142, 1129, 1075, 1052, 962, 878, 731 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 10.56 (s, 2H), 8.21 (s, 2H), 7.18 (t, J = 1.8 Hz, 2H), 7.11 (s, 4H), 6.93 (s, 1H), 6.14 (s, 4H), 2.95 (sept, J = 6.8 Hz, 2H), 2.58 (s, 3H), 2.34 (s, 6H), 2.26 (sept, J = 6.8 Hz, 4H), 1.28 (d, J = 6.8 Hz, 12H), 1.24 (d, J = 6.8 Hz, 12H), 1.15 (d, J = 6.8 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 152.6 (2C), 145.0 (4C), 140.1 (2C), 138.6, 138.2 (2C), 131.8 (2C), 128.5 (2C), 128.0, 125.0 (2C), 123.6 (2C), 122.5 (4C), 48.4 (2C), 34.5 (2C), 28.7 (4C), 24.6 (4C), 24.1 (4C), 23.9 (4C), 20.0 (2C), 16.8; HRMS (ESI) m/z calcld for [C₁₃H₁₆ClN₄]⁺ (M+Cl⁺): 721.4971; found: 721.4967.

1,1'-(2,4,6-Trimethyl-1,3-phenylene)bis(methylenecarbonyl)bis(3-(2,4,6-diisopropylphenyl)-1H-imidazol-3-ium) chloride (L8·2HCl)

Following general procedure A-(a), the reaction of 2,6-diisopropylaniline (9.43 mL, 50.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded L8·2HCl as a white solid (5.38 g, 71% Yield). Rf: 0.4 (MeOH/CH₂Cl₂ = 1/3); mp: 115-117 °C; IR (film): 2963, 2928, 2870, 1603, 1543, 1462, 1385, 1366, 1265, 1196, 1179, 1142, 1129, 1075, 1052, 962, 878, 731 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 10.56 (s, 2H), 8.21 (s, 2H), 7.18 (t, J = 1.8 Hz, 2H), 7.11 (s, 4H), 6.93 (s, 1H), 6.14 (s, 4H), 2.95 (sept, J = 6.8 Hz, 2H), 2.58 (s, 3H), 2.34 (s, 6H), 2.26 (sept, J = 6.8 Hz, 4H), 1.28 (d, J = 6.8 Hz, 12H), 1.24 (d, J = 6.8 Hz, 12H), 1.15 (d, J = 6.8 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 152.6 (2C), 145.0 (4C), 140.1 (2C), 138.6, 138.2 (2C), 131.8 (2C), 128.5 (2C), 128.0, 125.0 (2C), 123.6 (2C), 122.5 (4C), 48.4 (2C), 34.5 (2C), 28.7 (4C), 24.6 (4C), 24.1 (4C), 23.9 (4C), 20.0 (2C), 16.8; HRMS (ESI) m/z calcld for [C₁₃H₁₆ClN₄]⁺ (M+Cl⁺): 721.4971; found: 721.4967.
mmol) with glyoxal (40% aq, 5.5 mL, 50.0 mmol), NH₄Cl (5.35 g, 100.0 mmol) and formaldehyde (37% aq, 7.5 mL, 100.0 mmol), afforded 1-Arylimidazole 13c as a yellow solid (5.14 g, 45% Yield), Rf: 0.3 (EtOAc/Hexane = 1/5). The spectral data were identical with those reported in the literature.5

Following general procedure A-(b), the reaction of 1-Arylimidazole 13c (5.41 g, 20.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded L8·2HCl as a white solid (4.85 g, 72% Yield). Rf: 0.4 (MeOH/CH₂Cl₂ = 1/3); mp: 174-176 °C. IR (film): 2963, 2927, 2870, 1657, 1564, 1606, 1546, 1460, 1451, 1385, 1242, 1180, 1142, 1113, 1075, 876, 806, 760, 672, 628 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 10.64 (s, 2H), 8.58 (br s, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.31-7.29 (m, 2H), 7.28 (br s, 2H), 7.21-7.17 (m, 2H), 6.88 (s, 1H), 6.13 (s, 4H), 2.62 (s, 3H), 2.32 (s, 6H), 2.28 (sept, J = 6.6 Hz, 4H), 1.24 (d, J = 6.6 Hz, 12H), 1.15 (d, J = 6.8 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃): δ 145.3 (4C), 140.1 (2C), 138.6, 138.1 (2C), 131.9 (2C), 131.8, 130.3 (2C), 128.4 (2C), 124.9 (2C), 124.6 (4C), 124.2 (2C), 48.4 (2C), 28.7 (4C), 24.6 (4C), 24.1 (4C), 20.0 (2C), 17.0; HRMS (ESI) m/z calcd for [C₁₄H₁₄ClN₂]⁺ (M-Cl⁻): 637.4032; found: 637.4030.

1,1',1''-[(Benzene-1,2,4,5-tetrayltetraakis(methylene)]tetrakis[3-(2,6-diisopropylphenyl)-1H-imidazol-3-ium) bromide (L9·4HBr)

Following general procedure A-(b), the reaction of 1-Arylimidazole 13c (5.41 g, 20.0 mmol) with 1,2,4,5-tetrayltetraakis(bromomethyl)benzene (2.25 g, 5.0 mmol), afforded L9·4HBr as a white solid (4.63 g, 68% Yield). Rf: 0.4 (MeOH/CH₂Cl₂ = 1/3); mp: 174-176 °C. IR (film): 2964, 2870, 1591, 1545, 1461, 1385, 1367, 1274, 1180, 1142, 1116, 1074, 958, 937, 805, 758, 731, 672 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 10.69 (s, 4H), 9.06 (t, J = 1.6 Hz, 4H), 8.44 (s, 2H), 7.54 (t, J = 7.8 Hz, 4H), 7.32 (d, J = 7.8 Hz, 8H), 7.18 (t, J = 1.7 Hz, 4H), 6.54 (s, 8H), 2.31 (sept, J = 6.7 Hz, 8H), 1.26 (d, J = 6.8 Hz, 24H), 1.20 (d, J = 6.8 Hz, 24H); ¹³C NMR (125 MHz, CDCl₃): δ 145.4 (8C), 137.6 (4C), 134.7 (4C), 134.5 (4C), 132.1 (4C), 130.0 (2C), 125.4 (4C), 124.8 (8C), 124.5 (4C), 49.4 (4C), 28.9 (8C), 24.6 (8C), 24.1 (8C); HRMS (ESI) m/z calcd for [C₇₀H₈₀Br₃N₈]⁺ (M-Br⁻): 1283.4798; found 1283.4913.

3. Amides 1a–1t, 7–11,

The known amides 1a²⁻, 1b⁶, 1f⁹c, 1h⁷d, 1i⁷e, 1j⁷b, 1p⁷c, 1t⁷b, 7i², 8i² were synthesized according to general procedures B, while 9⁸ were synthesized according to general procedures D. The known amides 10⁹h, 11⁷i were synthesized according to literature procedure.⁷h

The unknown amides 1c–e, 1g, 1q–s were synthesized according to general procedures B, and the unknown amides 1n–o were synthesized according to general procedures C. Meanwhile, the unknown amides 1k–m were synthesized according to specific procedure as follows.

General procedure B for synthesis of N-acylpyrroles from acyl chlorides.

A previously published procedure was followed.⁷i
To a stirred solution of pyrrole (0.38 mL, 7.5 mmol, 1.5 equiv) in THF (10.0 mL) maintained at -78 °C under Argon was added dropwise n-BuLi (2.4 M in hexane, 3.1 mL, 1.5 equiv) and the solution was then stirred for 10 mins. After that, a solution of acyl chloride (5.0 mmol, 1.0 equiv) in THF (10.0 mL) was added. Then the reaction was slowly warmed to room temperature and stirred overnight. The reaction was diluted with EtOAc (10 mL), and washed with a saturated aqueous NaHCO₃ solution (10 mL) and brine (10 mL), and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired N-acylpyrrole.

**General procedure C for synthesis of N-acylpyrroles from primary amides.**

A previously published procedure was followed.⁷₆

![Chemical Reaction Diagram]

1) (COCl)₂, CH₂Cl₂
   0°C to RT, 4 h

2) NH₄H₂O, 1 h
   0°C to RT

(1) (a): Oxalyl chloride (0.85 mL, 10.0 mmol, 2.0 equiv) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid (5.0 mmol, 1.0 equiv) in CH₂Cl₂ (10.0 mL, 0.5 M) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride (prepared above) in anhydrous CH₂Cl₂ (10.0 mL, 0.5 M) was added dropwise to an aqueous ammonia solution (25%, 7.7 mL, 50.0 mmol, 10.0 equiv) at 0 °C. After stirring for 1 h, the precipitate was collected by suction-filtration, washed with water and n-hexane, and dried under reduced pressure. The crude solid was recrystallization from ethyl acetate to afford the desired primary amide.

(2) A mixture of primary amide (prepared above), 2,5-dimethoxymethylenehydrofuran (1.3 mL, 10.0 mmol, 2.0 equiv) in AcOH (10.0 mL, 0.5 M) was reflux for 12 h. Then the mixture was cooled, poured into ice, neutralized with NaHCO₃, and extracted with EtOAc (10 mL×3). The combined organic layer was filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to yield the desired N-acylpyrrole.

**General procedure D for synthesis of N-benzoyl(2,5-dimethyl)pyrrole from primary amides.**

A previously published procedure was followed.⁷₇
(1) (a): Oxalyl chloride (0.85 mL, 10.0 mmol, 2.0 equiv) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid (5.0 mmol, 1.0 equiv) in CH₂Cl₂ (10.0 mL, 0.5 M) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride (prepared above) in anhydrous CH₂Cl₂ (10.0 mL, 0.5 M) was added dropwise to an aqueous ammonia solution (25%, 7.7 mL, 50.0 mmol, 10.0 equiv) at 0 °C. After stirring for 1 h, the precipitate was collected by suction-filtration, washed with water and n-hexane, and dried under reduced pressure. The crude solid was recrystallized from ethyl acetate to afford the desired primary amide.

(2) A mixture of primary amide (prepared above), hexane-2,5-dione (1.3 mL, 11.0 mmol, 2.2 equiv) and TsOH·H₂O (95.1 mg, 0.5 mmol, 0.1 equiv) in Toluene (10.0 mL, 0.5 M) was stirred at 140 °C for 12 h. Then the mixture was cooled, poured into ice, neutralized with NaHCO₃, and extracted with EtOAc (10 mL×3). The combined organic layer was filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to yield the desired N-benzoyl(2,5-dimethyl)pyrrole.

(1H-Pyrrol-1-yl)(m-tolyl)methanone (1c)

Following general procedure B, the reaction of 3-methylbenzoyl chloride (0.66 mL, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the N-acylpyrrole 1c as a light yellow oil (759.3 mg, 82% Yield). Rf: 0.5 (EtOAc/Hexane = 1/20); IR (film): 2923, 1698, 1605, 1586, 1543, 1466, 1422, 1400, 1331, 1304, 1160, 1087, 1074, 1045, 917, 825, 812, 791, 737, 672 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.56 (s, 1H), 7.52 (dt, J = 7.2, 1.8 Hz, 1H), 7.43-7.34 (m, 2H), 7.28 (t, J = 2.3 Hz, 2H), 6.34 (t, J = 2.3 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 168.0, 138.5, 133.3, 133.1, 130.1, 128.4, 126.7, 121.4 (2C), 113.1 (2C), 21.4; HRMS (ESI) m/z calcd for [C₁₂H₁₂NNaO]⁺ (M+Na⁺): 208.0733; found: 208.0736.

(1H-Pyrrol-1-yl)(o-tolyl)methanone (1d)

Following general procedure B, the reaction of 2-methylbenzoyl chloride (0.65 mL, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the N-acylpyrrole 1d as a yellow oil (657.5 mg, 71% Yield). Rf: 0.5 (EtOAc/Hexane = 1/20); IR (film): 2926, 1706, 1603, 1544, 1467, 1399, 1329, 1305, 1255, 1084, 1073, 882, 796, 777, 738, 664 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.42 (td, J = 7.5, 1.2 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.32-7.26 (m, 2H), 7.14 (t, J = 2.3 Hz, 2H), 6.31 (t, J
Following **general procedure C**, the reaction of 4-((1R,4R)-4-ethylcyclohexyl) benzoic acid (1.16 g, 5.0 mmol), with an aqueous ammonia solution (25%, 7.7 mL, 50.0 mmol) and pyrrole (0.38 mL, 7.5 mmol), afforded the N-acetylpyrrole **1e** as a white solid (872.3 mg, 62% Yield, over two steps). Rf: 0.5 (EtOAc/Hexane = 1/20); mp: 51-53 °C; IR (film): 2959, 2921, 2851, 1697, 1608, 1448, 1415, 1400, 1331, 1299, 1255, 1180, 1088, 1073, 884, 846, 766, 741, 720, 680 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 2.3 Hz, 2H), 6.34 (t, J = 2.4 Hz, 2H), 2.56 (dt, J = 12.1, 3.3 Hz, 1H), 1.96-1.88 (m, 4H), 1.48 (qd, J = 12.7, 3.3 Hz, 2H), 1.32-1.24 (m, 2H), 1.24-1.18 (m, 1H), 1.12-1.02 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 167.8, 152.9, 130.7, 129.9 (2C), 127.1 (2C), 121.4 (2C), 112.9 (2C), 44.8, 39.1, 34.1 (2C), 33.1 (2C), 30.0, 11.6; HRMS (ESI) m/z calcd for [C₁₉H₁₅NNaO⁺] (M+Na⁺): 304.1672; found: 304.1674; [α]ᵦ₂⁰ = -0.36 (c 1.0, CHCl₃).

**1H-Pyrrol-1-yl)(3,4,5-trimethoxyphenyl)methanone (1g)**

Following **general procedure B**, the reaction of 3,4,5-trimethoxybenzoyl chloride (1.15 g, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the N-acetylpyrrole **1g** as a white solid (914.6 mg, 70% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp: 89-91 °C; IR (film): 3138, 3112, 2944, 2829, 1681, 1586, 1503, 1466, 1454, 1417, 1404, 1351, 1311, 1292, 1240, 1155, 1126, 1102, 995, 935, 812, 761, 742 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.32 (t, J = 2.2 Hz, 2H), 7.00 (s, 2H), 6.36 (t, J = 2.2 Hz, 2H), 3.94 (s, 3H), 3.90 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 167.2, 153.1 (2C), 141.6, 128.1, 121.4 (2C), 113.1 (2C), 107.2 (2C), 61.0, 56.4 (2C); HRMS (ESI) m/z calcd for [C₁₃H₁₅NNaO₂⁺] (M+Na⁺): 284.0893; found: 284.0894.

Synthesis of **N-acetylpyrrole 1m** from 2-phenylpropanoic acid **14**.

**N-(4-(1H-Pyrrole-1-carbonyl)phenyl)-N-methyl-2-phenylpropanamide (1k)**
(1) Oxalyl chloride (0.34 mL, 4.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid 14 (300.0 mg, 2.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. A solution of acyl chloride prepared above in anhydrous CH₂Cl₂ (4.0 mL) was added dropwise to a solution of Methyl 4-(methylamino)benzoate (496.0 mg, 3.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C. After stirring for 1 h, the precipitate was collected by suction filtration, washed with water (5 mL) and n-hexane (4×2 mL), and dried under reduced pressure. The crude product was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired amide 16 as a light yellow oil (481.6 mg, 81% yield). Rₘ: 0.4 (EtOAc/Hexane = 1/5); IR (film): 3027, 2930, 1724, 1663, 1603, 1507, 1492, 1452, 1435, 1376, 1331, 1279, 1114, 1101, 1021, 747, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, J = 8.1 Hz, 2H), 7.25-7.15 (m, 3H), 7.06 (d, J = 7.1 Hz, 2H), 7.01 (d, J = 7.1 Hz, 2H), 3.94 (s, 3H), 3.63 (s, 1H), 3.25 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 173.8, 166.3, 148.0, 141.6, 131.0 (2C), 128.6 (2C), 127.8 (2C), 127.5 (2C), 126.9 (2C), 52.4, 43.6, 37.7, 20.5; HRMS (ESI) m/z calcd for [C₁₈H₁₉NNaO₃]⁺ (M+Na⁺): 320.1257; found: 320.1258.

(2) To a reaction vessel equipped with a magnetic stir bar under Argon were added the substrate amide 16 (prepared above), CaCl₂ (179.8 mg, 1.62 mmol), and NH₃ (7 N in MeOH, 2.3 mL). The reaction vessel is sealed and heated at 80 °C for 24 h. Then the reaction mixture is concentrated and the residue is treated with saturated NH₄Cl solution (2.4 mL) and H₂O (2.4 mL). The resulting mixture is adjusted to pH 5 with 2N HCl and the mixture is stirred for 20 min to dissolve Ca salts, after which the precipitated amide is filtered, washed with H₂O (4 mL), and dried. The resulting crude primary amide was used in the next step without further purification.

(3) A mixture of primary amide 17 (prepared above), 2,5-dimethoxytetrahydrofuran (0.42 mL, 3.24 mmol) in AcOH (3.2 mL) was reflux for 12 h. The mixture was cooled, poured into ice, neutralized with NaHCO₃, and extracted with EtOAc (4 mL×2). The combined
organic layer was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired N-acylpyrrole 1k as a light oil (251.4 mg, 51% Yield, over two steps). Rf: 0.5 (EtOAc/Hexane = 1/5); IR (film): 2970, 2930, 2870, 1698, 1663, 1603, 1509, 1492, 1467, 1401, 1375, 1331, 1123, 1090, 1074, 1022, 976, 881, 857, 804, 771, 746, 701 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.71 (d, J = 7.7 Hz, 2H), 7.28 (t, J = 2.3 Hz, 2H), 7.25-7.17 (m, 3H), 7.12 (d, J = 7.3 Hz, 2H), 7.02 (d, J = 7.3 Hz, 2H), 6.39 (t, J = 2.3 Hz, 2H), 3.29 (s, 3H), 1.66-1.57 (m, 1H), 1.43 (d, J = 6.8 Hz, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): δ 173.6, 166.7, 147.3, 141.6 (2C), 130.7 (2C), 128.6 (2C), 127.8 (2C), 127.4 (2C), 126.9, 121.2 (2C), 113.5 (2C), 43.8, 37.7, 20.5; HRMS (ESI) m/z calcd for [C\(_{21}\)H\(_{20}\)N\(_2\)NaO\(_2\)]\(^+\) (M+Na\(^+\)): 355.1417; found: 355.1421.

Synthesis of N-acylpyrrole 1n from 4-(methoxycarbonyl)benzoic acid 18:

\( \text{N-Methyl-N-phenyl-4-(1H-pyrrole-1-carbonyl)benzamide (1I)} \)

\[
\begin{align*}
\text{18} & \xrightarrow{1} \text{19} \quad \text{(1)} \\
\text{19} & \xrightarrow{\text{CaCl}_2, \text{NH}_3\cdot\text{H}_2\text{O}} \text{1n} \\
\text{1n} & \xrightarrow{\text{AcOH}} \text{20}
\end{align*}
\]

(1) (a) Oxalyl chloride (0.34 mL, 4.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid 18 (360.4 mg, 2.0 mmol) in CH\(_2\)Cl\(_2\) (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride prepared above in anhydrous CH\(_2\)Cl\(_2\) (4.0 mL) was added dropwise to a solution of N-methylaniline (0.33 mL, 3.0 mmol) in CH\(_2\)Cl\(_2\) (4.0 mL) at 0 °C. After stirring for 1 h, the precipitate was collected by suction filtration, washed with water (5 mL) and \(n\)-hexane (4×2 mL), and dried under reduced pressure. The crude solid was recrystallized from ethyl acetate to afford the desired amide 19 as a white solid (447.0 mg, 83% Yield). Rf: 0.5 (EtOAc/Hexane = 1/5); mp: 113-115 °C; IR (film): 3061, 2951, 1723, 1644, 1595, 1496, 1435, 1371, 1279, 1108, 1020, 865, 771, 736, 723, 700 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.83 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H), 3.86 (s, 3H), 3.51 (s, 3H); \(^13\)C NMR (500 MHz, CDCl\(_3\)): δ 169.8, 166.4, 144.3, 140.3, 130.9, 129.4 (2C), 129.1 (2C), 128.6 (2C), 127.0
(3C), 52.3, 38.4; MS (ESI) m/z 270 (M+H^+, 100%).

(2) To a reaction vessel equipped with a magnetic stir bar under Argon were added the amide 19 (prepared above), CaCl₂ (184.0 mg, 1.66 mmol) and NH₃ (7 N in MeOH, 2.4 mL). The reaction vessel was sealed and heated at 80 °C for 24 h. Then the reaction mixture is concentrated and the residue is treated with saturated NH₄Cl (2.5 mL) solution and H₂O (2.5 mL). The resulting mixture is adjusted to pH 5 with 2N HCl and the mixture is stirred for 20 min to dissolve Ca salts, after which the precipitated amide is filtered, washed with H₂O (4 mL), and dried. The resulting crude primary amide was used in the next step without further purification.

(3) A mixture of primary amide 20 (prepared above), 2,5-dimethoxytetrahydrofuran (0.4 mL, 3.32 mmol) in AcOH (3.3 mL) was reflux for 12 h. The mixture was cooled, poured into ice, neutralized with NaHCO₃ and washed with EtOAc (4 mL×2). The combined organic layer was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired N-aclypyrrole 11 as a white solid (252.6 mg, 50% Yield, over two steps). Rf: 0.5 (EtOAc/Hexane = 1/5); mp: 112-114 °C; IR (film): 3060, 2927, 1697, 1644, 1595, 1564, 1495, 1467, 1403, 1371, 1331, 1301, 1196, 1176, 1090, 1075, 1030, 975, 886, 871, 856, 743, 700, 574 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.54 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.20-7.12 (m, 3H), 7.05 (d, J = 7.6 Hz, 2H), 6.31 (d, J = 2.3 Hz, 2H), 3.53 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 169.4, 167.0, 144.3, 139.8, 134.0, 129.5 (2C), 129.0 (2C), 128.7 (2C), 127.2, 127.0 (2C), 121.2 (2C), 113.4 (2C), 38.4; HRMS (ESI) m/z calcd for [C₁₉H₁₆N₂NaO₂⁺] (M+Na⁺): 327.1104; found: 327.1103.

Synthesis of N-aclypyrrole 10 from 4-(methoxycarbonyl)benzoic acid 18.

**N-(2,6-Dimethylphenyl)-4-(1H-pyrrole-1-carbonyl)benzamide (1m)**

![Chemical structure of 1m](image1)

(a) Oxalyl chloride (0.34 mL, 4.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid 18 (360.4 mg, 2.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the
reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride prepared above in anhydrous CH₂Cl₂ (4.0 mL) was added dropwise to a solution of 2,6-Dimethylaniline (0.37 mL, 3.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C. After stirring for 1 h, the precipitate was collected by suction filtration, washed with water (5 mL) and n-hexane (5 mL), and dried under reduced pressure. The crude solid was recrystallization from ethyl acetate to afford the desired amide 21 as a light yellow solid (425.0 mg, 75% Yield). Rf: 0.5 (EtOAc c/Hexane = 1/5); mp: 192-194 °C; IR (film): 3097, 2953, 2919, 1721, 1645, 1613, 1572, 1529, 1497, 1439, 1283, 1193, 1123, 1110, 1016, 821, 777, 730 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.12 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.2 Hz, 2H), 7.59 (s, 1H), 7.18-7.09 (m, 3H), 3.96 (s, 3H), 2.26 (s, 6H); ¹³C NMR (500 MHz, CDCl₃): δ 166.3, 165.2, 138.4, 135.6 (2C), 133.6, 133.0, 130.1 (2C), 128.4 (2C), 127.7, 127.3 (2C), 52.5, 18.5 (2C); HRMS (ESI) m/z calcd for [C₁₂H₁₇NNaO₃]^+ (M+Na⁺): 306.1101; found: 306.1100.

(2) A solution of LiOH (96 mg, 3.0 mmol) in water (15.0 mL) was added to the solution of amide 21 (prepared above) in THF (15.0 mL). After refluxing for 1 h, the reaction mixture was adjusted to acidic by 2N HCl, and then extracted with EtOAc (15 mL×3). The organic phase was concentrated under reduced pressure. The resulting crude carboxylic acid 22 was used in the next step without further purification.

(3) (a) Oxaly chloride (0.34 mL, 3.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid 22 (prepared above) in CH₂Cl₂ (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. b): To a stirred solution of pyrrole (0.16 mL, 2.3 mmol) in THF (3.0 mL) maintained at −78 °C under Argon was added dropwise n-BuLi (2.4 M in hexane, 1.0 mL) and the solution was then stirred for 10 mins. After that, a solution of acyl chloride (prepared above) in THF (3.0 mL) was added. Then the reaction was slowly warmed to room temperature, and stirred overnight. The reaction was diluted with EtOAc (5 mL), and washed with a saturated aqueous NaHCO₃ solution (5 mL) and brine (5 mL), and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexanes = 1/5) to yield the desired N-acylpyrrole 1m as a white solid (195.8 mg, 41% Yield, over two steps). Rf: 0.5 (EtOAc/Hexane = 1/5); mp: The compound decomposed at 194 °C; IR (film): 2923, 2853, 1698, 1648, 1522, 1495, 1467, 1403, 1332, 1301, 1196, 1132, 1088, 1076, 1019, 881, 771, 730 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, J = 7.9 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.62 (s, 1H), 7.27 (t, J = 2.3 Hz, 2H), 7.20-7.09 (m, 3H), 6.39 (t, J = 2.3 Hz, 2H), 2.29 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 166.9, 164.9, 137.8, 136.3, 135.6, 133.6, 129.8 (2C), 128.5 (2C), 127.8 (2C), 127.5 (2C), 121.2 (2C), 113.8 (2C), 18.5 (2C); HRMS (ESI) m/z calcd for [C₂₀H₁₈N₂NaO₃]^+ (M+Na⁺): 341.1261; found: 341.1265.

(4-(4-Methylpiperazin-1-yl)phenyl)(1H-pyrrol-1-yl)methanone (1n)
Following general procedure C, the reaction of 4-(4-methylpiperazin-1-yl)benzoic acid (1.16 g, 5.0 mmol) with an aqueous ammonia solution (25%, 7.7 mL, 50 mmol) and 2,5-dimethoxytetrahydrofuran (1.3 mL, 10 mmol), afforded the N-acylpyrrole 1n as a yellow solid (686.7 mg, 51% Yield, over two steps). Rf: 0.3 (EtOAc/Hexane = 1/2); mp: 91-93 °C; IR (film): 2936, 2796, 1681, 1604, 1518, 1464, 1398, 1382, 1330, 1296, 1246, 1182, 1142, 1008, 924, 882, 764, 774 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.72 (d, \(J = 8.8\) Hz, 2H), 7.31 (t, \(J = 2.3\) Hz, 2H), 6.92 (t, \(J = 8.9\) Hz, 2H), 6.32 (t, \(J = 2.3\) Hz, 2H), 3.39 (t, \(J = 5.0\) Hz, 4H), 2.58 (t, \(J = 5.0\) Hz, 4H), 2.37 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 167.3, 153.9, 132.1 (2C), 122.2, 121.5 (2C), 113.7 (2C), 112.4 (2C), 54.8 (2C), 47.4 (2C), 46.2; HRMS (ESI) \(m/z\) calcd for [C\(_{16}\)H\(_{15}\)N\(_3\)NaO]\(^+\) (M+Na\(^+\)) : 292.1420; found: 292.1420.

**(4-Morpholinophenyl)(1H-pyrrol-1-yl)methanone (1o)**

Following general procedure C, the reaction of 4-morpholinobenzoic acid (1.04 g, 5.0 mmol) with an aqueous ammonia solution (25%, 7.7 mL, 50 mmol) and 2,5-dimethoxytetrahydrofuran (1.3 mL, 10 mmol), afforded the N-acylpyrrole 1o as a yellow solid (692.0 mg, yield: 54%). Mp: 112-114 °C; IR (film): 2960, 2921, 2852, 1682, 1603, 1517, 1465, 1449, 1398, 1383, 1330, 1296, 1242, 1182, 1123, 1088, 1073, 928, 882, 831, 764, 743, 659 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.74 (d, \(J = 8.8\) Hz, 2H), 7.31 (d, \(J = 2.2\) Hz, 2H), 6.92 (d, \(J = 8.7\) Hz, 2H), 6.33 (t, \(J = 2.2\) Hz, 2H), 3.87 (t, \(J = 4.8\) Hz, 4H), 3.32 (t, \(J = 4.8\) Hz, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 167.3, 154.0, 132.1 (2C), 122.7, 121.4 (2C), 113.5 (2C), 112.5 (2C), 66.6 (2C), 47.7 (2C); HRMS (ESI) \(m/z\) calcd for [C\(_{15}\)H\(_{16}\)N\(_2\)NaO\(_2\)]\(^+\) : 279.1104; found: 279.1105.

**Furan-3-yl(1H-pyrrol-1-yl)methanone (1q)**

Following general procedure B, the reaction of furan-3-carbonyl chloride (0.49 mL, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the N-acylpyrrole 1q as a light yellow solid (523.9 mg, 65% Yield). Rf: 0.5 (EtOAc/Hexane = 1/20); mp: 33-36 °C; IR (film): 3149, 2920, 1693, 1642, 1565, 1504, 1467, 1405, 1381, 1343, 1259, 1238, 1180, 1162, 1142, 1103, 1075, 1020, 876, 838, 739, 600 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.02 (dd, \(J = 1.6, 0.8\) Hz, 1H), 7.53 (t, \(J = 1.7\) Hz, 1H), 7.40 (t, \(J = 2.3\) Hz, 2H), 6.85 (dd, \(J = 1.9, 0.8\) Hz, 1H), 6.36 (t, \(J = 2.3\) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 161.2, 147.3, 144.0, 120.7, 120.5 (2C), 113.4 (2C), 110.9; HRMS (ESI) \(m/z\) calcd for [C\(_{9}\)H\(_{7}\)NNaO\(_2\)]\(^+\) (M+Na\(^+\)) : 184.0369; found: 184.0370.
(1H-Pyrrol-1-yl)(thiophen-3-yl)methanone (1r)

Following **general procedure B**, the reaction of thiophene-3-carbonyl chloride (733.0 mg, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the N-acetylpyrrole 1r as a yellow oil (487.4 mg, yield: 55%). IR (film): 3106, 2924, 2863, 1686, 1605, 1584, 1534, 1516, 1466, 1451, 1412, 1325, 1297, 1247, 1200, 1151, 1075, 1044, 881, 844, 815, 750, 737 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.02 (dd, J = 1.5, 0.8 Hz, 1H), 7.53 (t, J = 1.7 Hz, 1H), 7.40 (t, J = 2.3 Hz, 2H), 6.85 (dd, J = 1.9, 0.8 Hz, 1H), 6.36 (t, J = 2.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 161.2, 147.3, 144.0, 120.7, 120.5 (2C), 113.4 (2C), 110.9; HRMS (ESI) m/z calcd for [C₉H₇NNaOS]+: 200.0141; found: 200.0146.

(4-Iodophenyl)(1H-pyrrol-1-yl)methanone (1s)

Following **general procedure B**, the reaction of 4-iodobenzoyl chloride (1.33 g, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the N-acetylpyrrole 1s as a white solid (1.23 g, 83% Yield). Rf: 0.5 (EtOAc/Hexane = 1/20); mp: 73-74 °C; IR (film): 3031, 2917, 2849, 1694, 1584, 1467, 1401, 1392, 1331, 1298, 1090, 1075, 1008, 878, 838, 740, 681 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.25 (t, J = 2.2 Hz, 2H), 6.36 (t, J = 2.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 167.0, 137.9 (2C), 132.7, 131.0 (2C), 121.2 (2C), 113.6 (2C), 99.7; HRMS (ESI) m/z calcd for [C₁₁H₈INNaO]⁺ (M+Na⁺): 319.9543; found: 319.9544.

4. The scope of amides and neopentyl glycol esters

**General procedure E** for coupling of N-acetylpyrrole 1 and (hetero)arylboronic acid neopentyl glycol esters 2 to yield ketones 3.

A vial packaged with tin foil was charged with powdered K₂PO₄ (101.9 mg, 0.48 mmol, 2.0 equiv), N-acetylpyrrole 1 (0.24 mmol, 1.0 equiv), (hetero)arylboronic acid neopentyl glycol ester 2 (0.48 mmol, 2.0 equiv), L₈-2HCl (16.2 mg, 0.024 mmol, 10 mol%) and a magnetic stir bar. Then, the vial was taken into a glove box and charged with Ni(COD)₂ (6.6mg, 0.024 mmol, 10 mol%). After that, toluene (0.5 mL, 0.5 M) and water (8.6 uL, 0.48 mmol, 2.0 equiv) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 60°C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (1 mL), washed with a saturated aqueous Na₂CO₃ solution (1 mL) and brine (1.0 mL), and then dried over anhydrous Na₂SO₄. The combined organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the desired ketone 3.

(4-Methoxyphenyl)(phenyl)methanone (3aa)
Following general procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3aa\(^{ab}\) as a white solid (47.9 mg, 94% Yield). Rr: 0.4 (EtOAc/Hexane = 1/10); mp: 60-62 °C; IR (film): 2933, 2839, 1653, 1599, 1577, 1508, 1445, 1419, 1317, 1281, 1257, 1172, 1148, 1029, 938, 923, 844, 793, 741 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 8.8\) Hz, 2H), 7.75 (d, \(J = 7.8\) Hz, 2H), 7.56 (t, \(J = 7.3\) Hz, 1H), 7.46 (t, \(J = 7.6\) Hz, 2H), 6.96 (d, \(J = 8.8\) Hz, 2H), 3.88 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 195.6, 163.3, 138.3, 132.6 (2C), 131.9, 130.2, 129.8 (2C), 128.2 (2C), 113.6 (2C), 55.5; MS (ESI) \(m/z\) 213 (M+H\(^+\), 100%).

4-Methoxyphenyl)(\(\rho\)-tolyl)methanone (3ba)

Following general procedure E, the reaction of N-acylpyrrole 1b (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ba\(^{ab}\) as a light yellow solid (50.0 mg, 92% Yield). Rr: 0.4 (EtOAc/Hexane = 1/10); mp: 89-90 °C; IR (film): 3148, 2920, 2850, 1697, 1609, 1543, 1504, 1466, 1401, 1329, 1303, 1089, 1074, 882, 832, 740 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.81 (d, \(J = 8.8\) Hz, 2H), 7.68 (d, \(J = 8.0\) Hz, 2H), 7.27 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 8.8\) Hz, 2H), 3.88 (s, 3H), 3.44 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 195.4, 163.1, 142.7, 135.6, 132.5 (2C), 130.6, 130.1 (2C), 128.9 (2C), 113.6 (2C), 55.5, 21.7; MS (ESI) \(m/z\) 186 (M+H\(^+\), 100%).

(4-Methoxyphenyl)(\(m\)-tolyl)methanone (3ca)

Following general procedure E, the reaction of N-acylpyrrole 1c (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ca\(^{ab}\) as a white solid (50.5 mg, 93% Yield). Rr: 0.4 (EtOAc/Hexane = 1/10); mp 53-54 °C; IR (film): 2920, 1651, 1598, 1572, 1508, 1460, 1420, 1313, 1286, 1258, 1170, 1030, 960, 846, 755, 712 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.82 (d, \(J = 8.8\) Hz, 2H), 7.57 (s, 1H), 7.53 (d, \(J = 7.2\) Hz, 1H), 7.39-7.32 (m, 2H), 6.96 (d, \(J = 8.7\) Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 195.9, 163.2, 138.4, 138.1, 132.7, 132.6 (2C), 130.4, 130.2, 128.1, 127.0, 113.6 (2C), 55.5, 21.4; MS (ESI) \(m/z\) 227 (M+H\(^+\), 100%).

(4-Methoxyphenyl)(\(o\)-tolyl)methanone (3da)

Following general procedure E, the reaction of N-acylpyrrole 1d (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3da\(^{ac}\)
as a colorless oil (28.8 mg, 53% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); IR (film): 2924, 1656, 1599, 1574, 1508, 1456, 1314, 1292, 1258, 1179, 1149, 1028, 926, 846, 750 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 7.79 (d, J = 8.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.30-7.26 (m, 2H), 7.24 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.30 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 197.5, 163.8, 139.3, 136.2, 132.6 (2C), 130.9, 130.6, 129.9, 128.0, 125.2, 113.8 (2C), 55.6, 19.9; MS (ESI) m/z 227 (M+H⁺, 100%).

(4-({1R,4R}-4-Ethylcyclohexyl)phenyl)(4-methoxyphenyl)methanone (3ea)

Following general procedure E, the reaction of N-aclypyrrole 1e (67.5 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ea as a white solid (63.4 mg, 82% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp:71-72 °C; IR (film): 2919, 2849, 1650, 1603, 1509, 1446, 1416, 1312, 1281, 1256, 1180, 1171, 1142, 1076, 1029, 929, 852, 769 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, J = 8.9 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.51-2.59 (m, 1H), 1.87-1.96 (m, 4H), 1.44-1.54 (m, 2H), 124-1.32 (m, 2H), 1.17-1.24 (m, 1H), 1.12-1.02 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 195.4, 163.0, 152.4, 135.9, 132.5 (2C), 130.5, 130.1 (2C), 126.7 (2C), 113.5 (2C), 55.5, 44.8, 39.0, 34.1 (2C), 33.1 (2C), 30.0, 11.5; HRMS (ESI) m/z calcd for [C₂₂H₂₆NaO₂⁺]⁺ (M+Na⁺): 345.1825; found: 345.1826. [α]D20 0.24 (c 0.5, CHCl₃).

Bis(4-methoxyphenyl)methanone (3fa)

Following general procedure E, the reaction of N-aclypyrrole 1f (48.3 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded 3fa as a pale yellow solid (48.3 mg, 83% Yield). Rf: 0.4 (EtOAc/PE = 1/10); mp: 129-135°C; IR (film): 2965, 2917, 2843, 1636, 1605, 1503, 1417, 1314, 1255, 1181, 1150, 1076, 1026, 851, 765, 687 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 8.6 Hz, 4H), 6.96 (d, J = 8.7 Hz, 4H), 3.89 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 194.6, 162.9 (2C), 132.3 (4C), 130.8 (2C), 113.5 (4C), 55.5 (2C); MS (ESI) m/z 243 (M+H⁺, 100%).

(4-Methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (3ga)

Following general procedure E, the reaction of N-aclypyrrole 1g (62.7 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ga as a...
as a colorless oil (58.0 mg, 80% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); IR (film): 3052, 2936, 2838, 1648, 1600, 1581, 1508, 1459, 1412, 1333, 1254, 1232, 1169, 1125, 1027, 998, 845, 765 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 7.83 (d, J = 8.6 Hz, 2H), 7.03 (s, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.88 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 194.7, 163.2, 152.9 (2C), 141.7, 133.4, 132.5 (2C), 130.3, 113.6 (2C), 107.5 (2C), 61.0, 56.4 (2C), 55.6; MS (ESI) m/z 325 (M+Na⁺, 100%).

(4-Fluorophenyl)(4-methoxyphenyl)methanone (3ha)

Following general procedure E, the reaction of N-acylpyrrole 1h (45.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ha as a white solid (47.5 mg, 86% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp: 91-92 °C; IR (film): 2917, 2847, 1641, 1603, 1501, 1384, 1261, 1180, 1148, 1076, 1030, 857, 842, 765, 682 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (t, J = 2.5 Hz, 2H), 7.79 (t, J = 2.5 Hz, 2H), 7.15 (t, J = 8.6 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 194.2, 165.1 (d, J = 253.3 Hz), 163.3, 134.5 (d, J = 3.6 Hz), 132.5 (2C), 132.4 (d, J = 9.1 Hz, 2C), 130.1, 115.4 (d, J = 22.1 Hz, 2C), 113.7 (2C), 55.6; MS (ESI) m/z 253 (M+Na⁺, 100%).

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (3ia)

Following general procedure E, the reaction of N-acylpyrrole 1i (57.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ia as a white solid (59.9 mg, 89% Yield). Rf: 0.4 (eluent: EtOAc/Hexane = 1/10); mp: 123-124 °C. IR (film): 2969, 1727, 1644, 1602, 1574, 1509, 1460, 1407, 1328, 1265, 1168, 1131, 1068, 1030, 1017, 862, 844, 771, 686 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 7.81-7.79 (m, 4H), 7.74 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 194.4, 163.8, 141.6, 133.3 (q, J = 32.6 Hz), 132.7 (2C), 129.9 (2C), 129.4, 125.3 (q, J = 3.7 Hz, 2C), 123.8 (q, J = 272.7 Hz), 113.9 (2C), 55.6; MS (ESI) m/z 281 (M+H⁺, 100%).

Methyl 4-(4-methoxybenzoyl)benzoate (3ja)

Following general procedure E, the reaction of N-acylpyrrole 1j (55.0 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ja (30.5 mg, 47% Yield) as a white solid. Mp: 160-162 °C. IR (film): 3011, 2918, 2848, 1716, 1641, 1602, 1433, 1405, 1284, 1255, 1146, 1107, 1026, 873, 844, 745, 709 cm⁻¹; ¹H NMR (500 MHz,
CDCl₃): δ 8.14 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.97 (s, 3H), 3.90 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 194.8, 166.4, 163.7, 142.2, 132.8, 132.6 (2C), 129.6, 129.5 (4C), 113.8 (2C), 55.6, 52.4; MS (ESI) m/z 271 (M+H⁺, 100%).

**N-(4-(4-Methoxybenzoyl)phenyl)-N-methyl-2-phenylpropanamide (3ka)**

Following general procedure E, the reaction of N-acylpyrrole 1k (79.8 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3ka as a light yellow oil (78.9 mg, 88% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); IR (film): 2970, 2931, 2839, 1656, 1600, 1509, 1454, 1419, 1377, 1314, 1279, 1257, 1171, 1149, 1122, 1025, 929, 860, 843, 775, 700, 688 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 7.9 Hz, 2H), 7.26-7.16 (m, 3H), 7.10 (d, J = 7.3 Hz, 2H), 7.05 (d, J = 7.3 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 3.29 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H), 1.26 (t, J = 7.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 194.4, 173.8, 163.6, 147.0, 141.8, 132.6 (2C), 131.0 (2C), 129.8, 128.6 (2C), 127.5 (4C), 126.8 (2C), 113.8 (2C), 55.6, 43.7, 37.8, 20.5; HRMS (ESI) m/z calcd for [C₂₂H₂₃NaO₃]⁺ (M+Na⁺): 396.1570; found: 396.1572.

**4-(4-Methoxybenzoyl)-N-methyl-N-phenylbenzamide (3la)**

Following general procedure E, the reaction of N-acylpyrrole 1l (73.0 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3la as a light yellow oil (64.7 mg, 78% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); IR (film): 2919, 2850, 1650, 1596, 1495, 1418, 1383, 1315, 1258, 1180, 1143, 1076, 1029, 930, 876, 860, 748, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.24 (t, J = 7.4 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.53 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 194.9, 169.9, 163.5, 144.4, 139.3, 139.0, 132.6 (2C), 129.8, 129.4 (2C), 129.2 (2C), 128.5 (2C), 127.0 (3C), 113.7 (2C), 55.6, 38.5; HRMS (ESI) m/z calcd for [C₂₃H₂₃NaO₃]⁺ (M+Na⁺): 368.1257; found: 368.1260.

**N-(2,6-Dimethylphenyl)-4-(4-methoxybenzoyl)benzamide (3ma)**

Following general procedure E, the reaction of N-acylpyrrole 1m (76.4 mg, 0.24 mmol) with
arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the ketone 3ma as a light yellow solid (65.6 mg, 76% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); mp: The compound decomposed at 189 °C; IR (film): 2923, 2852, 1650, 1599, 1511, 1493, 1316, 1282, 1259, 1195, 1173, 1149, 1132, 1077, 1027, 930, 843 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 6.3 Hz, 2H), 7.84 (d, J = 6.9 Hz, 2H), 7.46 (s, 1H), 7.19-7.12 (m, 3H), 6.99 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 194.7, 165.2, 163.7, 141.4, 137.3, 135.6 (2C), 133.7, 132.7 (2C), 130.0 (2C), 129.7, 128.5 (2C), 127.8, 127.2 (2C), 113.9 (2C), 55.7, 18.6 (2C); HRMS (ESI) m/z calcd for [C₂₃H₂₁NNaO₃]⁺ (M+Na⁺): 382.1414; found: 382.1414.

(4-Methoxyphenyl)(4-(4-methylpiperazin-1-yl)phenyl)methanone (3na)

Following the general procedure E (except the T = 80 °C), the reaction of N-acylpyrrole 1n (64.6 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3na as a light yellow oil (36.5 mg, 49% Yield). Rf: 0.4 (EtOAc); IR (film): 2934, 2846, 2797, 1636, 1601, 1559, 1541, 1516, 1456, 1381, 1291, 1241, 1180, 1170, 1142, 1076, 1029, 1009, 924, 770, 685 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.80-7.74 (m, 4H), 6.95 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 3.95 (t, J = 5.1 Hz, 4H), 2.60 (t, J = 5.0 Hz, 4H), 2.38 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 194.3, 162.6, 153.7, 132.3 (2C), 132.1 (2C), 131.3, 128.1, 113.6 (2C), 113.4 (2C), 55.5, 54.8 (2C), 47.5 (2C), 46.1. HRMS (ESI) m/z calcd for [C₁₅H₁₃N₃O₃]⁺ (M+Na⁺): 311.1754; found: 311.1755.

(4-Methoxyphenyl)(4-morpholinophenyl)methanone (3oa)

Following the general procedure E (except the T = 80 °C), the reaction of N-acylpyrrole 1o (61.5 mg, 0.24 mmol) and arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3oa as a light yellow solid (31.4 mg, 44% Yield). Rf: 0.5 (EtOAc); mp: 144-146 °C; IR (film): 2921, 2851, 1640, 1600, 1510, 1448, 1318, 1257, 1237, 1170, 1123, 1027, 926, 768 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 7.80-7.75 (m, 4H), 6.96 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.87 (t, J = 5.0 Hz, 4H), 3.32 (t, J = 5.0 Hz, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 194.3, 162.7, 153.9, 132.2 (2C), 132.1 (2C), 131.2, 128.6, 113.5 (2C), 113.4 (2C), 66.7 (2C), 55.5, 47.8 (2C); HRMS (ESI) m/z calcd for [C₁₆H₁₅NNaO₃]⁺: 320.1257; found: 320.1258.

(4-Methoxyphenyl)(naphthalen-2-yl)methanone (3pa)
Following general procedure E, the reaction of N-acetylpyrrole 1p (53.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3pa as a white solid (43.4 mg, 69% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp: 90-92 °C; IR (film): 2918, 2849, 1650, 1601, 1537, 1442, 1384, 1258, 1180, 1142, 1076, 877, 764, 637 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 8.23 (s, 1H), 7.95-7.86 (m, 6H), 7.62-7.52 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 195.6, 163.3, 135.6, 135.1, 132.7 (2C), 132.3, 131.2, 130.5, 129.3, 128.2, 128.1, 127.9, 126.8, 125.9, 113.7 (2C), 55.6; MS (ESI) m/z 263 (M+H⁺, 100%).

**Furan-3-yl(4-methoxyphenyl)methanone (3qa)**

Following general procedure E (except the T = 80 °C), the reaction of N-acetylpyrrole 1q (38.7 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3qa as a white solid (26.2 mg, 54% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp: 74-76 °C; IR (film): 2979, 2919, 1644, 1607, 1559, 1507, 1455, 1329, 1157, 1112, 1016, 872, 842, 762, 707 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.91 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 1.6 Hz, 1H), 6.98 (d, J = 8.6 Hz, 2H), 6.88 (s, 1H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 188.1, 163.3, 147.8, 143.8, 131.6, 131.3 (2C), 126.6, 113.9 (2C), 110.5, 55.6; HRMS (ESI) m/z calcld for [C₁₂H₁₀NaO₃⁺]⁺ (M+Na⁺): 225.0522; found: 225.0526.

**(4-Methoxyphenyl)(thiophen-3-yl)methanone (3ra)**

Following general procedure E (except the T = 80 °C), the reaction of N-acetylpyrrole 1r (42.5 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded ketone 3ra as a white solid. Mp: 67-69 °C. IR (film): 3112, 2918, 2848, 1639, 1598, 1573, 1507, 1419, 1386, 1310, 1277, 1256, 1170, 1138, 1026, 859, 843, 754, 702 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 7.95-7.83 (m, 3H), 7.56 (d, J = 5.0 Hz, 1H), 7.38 (dd, J = 5.1, 2.9 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 188.9, 163.2, 141.6, 132.8, 131.9 (2C), 131.2, 128.7, 126.0, 113.7 (2C), 55.5; MS (ESI) m/z 241 (M+Na⁺, 100%).

**Benzophenone (3ab)**

Following general procedure E, the reaction of N-acetylpyrrole 1a (41.1 mg, 0.24 mmol) with
arylboronic acid neopentyl glycol ester 2b (91.2 mg, 0.48 mmol), afforded ketone 3ab<sup>8a</sup> as a white solid (39.4 mg, 90% Yield). R<sub>t</sub>: 0.4 (EtOAc/Hexane = 1/20); mp: 47-48 °C; IR (film): 3059, 2918, 1659, 1598, 1577, 1447, 1317, 1277, 1179, 1142, 1075, 1028, 1000, 941, 919, 763, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.45-7.50 (m, 4H), 7.56-7.62 (m, 2H), 7.77-7.83 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 196.8, 137.7 (2C), 132.5 (2C), 128.3 (4C), 130.1 (4C); MS (ESI) m/z 205 (M+Na<sup>+</sup>, 100%).

**Phenyl(p-toly1)methanone (3ac)**

![Phenyl(p-toly1)methanone (3ac) structure](image)

Following general procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2c (98.0 mg, 0.48 mmol), afforded ketone 3ac<sup>8b</sup> as a white solid (42.9 mg, 91% Yield). R<sub>t</sub>: 0.4 (EtOAc/Hexane = 1/20); mp: 51-53 °C; IR (film): 3060, 2919, 1656, 1605, 1446, 1385, 1276, 1180, 1142, 1076, 922, 730, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.80-7.77 (m, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.58 (td, J = 7.4, 1.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 8.1 Hz, 2H), 2.44 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 196.6, 143.3, 138.0, 135.0, 132.2, 130.4 (2C), 130.0 (2C), 129.1 (2C), 128.3 (2C), 21.7; MS (ESI) m/z 197 (M+H<sup>+</sup>, 100%).

**(4-{(tert-Butyl)phenyl})(phenyl)methanone (3ad)**

![**(4-{(tert-Butyl)phenyl})(phenyl)methanone (3ad) structure](image)

Following general procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2d (118.2 mg, 0.48 mmol), afforded ketone 3ad<sup>8h</sup> as a white solid (53.2 mg, 93% Yield). R<sub>t</sub>: 0.4 (EtOAc/Hexane = 1/20); mp: 38-39 °C; IR (film): 3060, 2963, 1659, 1605, 1447, 1406, 1364, 1316, 1278, 1105, 939, 850, 702, 668 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.80 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 8.3 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.52-7.44 (m, 4H), 1.36 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 196.5, 156.2, 137.9, 134.8, 132.2, 130.2 (2C), 130.0 (2C), 128.2 (2C), 125.3 (2C), 35.1, 31.2 (3C); MS (ESI) m/z 239 (M+H<sup>+</sup>, 100%).

**(2-Methoxyphenyl)(phenyl)methanone (3ae)**

![**(2-Methoxyphenyl)(phenyl)methanone (3ae) structure](image)

Following General procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2e (105.6 mg, 0.48 mmol), afforded ketone 3ae<sup>8d</sup> (36.7 mg, 36% Yield; recover SM: 68.5 mg) after FC (eluent: EtOAc/PE = 1/10) as a white solid. Mp: 30-32 °C; IR (film): 2941, 1666, 1599, 1581, 1487, 1462, 1449, 1435, 1316, 1259, 1180, 1023, 925, 755, 702, 636 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.83-7.78 (m, 2H), 7.57-7.52 (m, 1H), 7.49-7.44 (m, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.36 (dd, J = 7.4, 1.8 Hz, 1H), 7.04 (td, J = 7.5, 1H).
0.8 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 3.72 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz): 196.5, 157.4, 137.9, 133.0, 131.9, 129.9 (2C), 129.6, 128.9, 128.3 (2C), 120.6, 111.5, 55.7; MS (ESI) m/z 235 (M+Na$^+$, 100%).

**4-Fluorophenyl)(phenyl)methanone (3af)**

Following general procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2f (99.8 mg, 0.48 mmol), afforded ketone 3af$^{4b}$ as a white solid (38.0 mg, 79% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); mp: 48-49 °C; IR (film): 3061, 2919, 1647, 1598, 1504, 1446, 1407, 1298, 1230, 1149, 1097, 940, 851, 735, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.85 (dd, J = 8.7, 5.5 Hz, 2H), 7.77 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.16 (t, J = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 115.5 (d, J = 22.0 Hz), 128.4 (2C), 129.9 (2C), 132.5 (2C), 132.7 (d, J = 9.2 Hz, 2C), 133.8 (d, J = 3.4 Hz), 137.5, 165.4 (d, J = 255.1 Hz), 195.3; MS (ESI) m/z: 201 (M+H$^+$, 100%).

**Phenyl(4-(trifluoromethyl)phenyl)methanone (3ag)**

Following general procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2g (123.8 mg, 0.48 mmol), afforded ketone 3ag$^{8d}$ as a white solid (42.6 mg, 71% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); mp: 115-116 °C; IR (film): 3052, 2919, 1651, 1598, 1447, 1408, 1335, 1276, 1169, 1134, 1117, 1068, 857, 750, 696 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.89 (d, J = 8.1 Hz, 2H), 7.83-7.79 (m, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 7.6, 1.3 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 194.6, 139.8, 135.8, 132.8 (q, J = 33.0 Hz), 132.2, 129.2 (2C), 129.1 (2C), 127.6 (2C), 124.4 (q, J = 3.8 Hz, 2C), 122.8 (q, J = 272.3 Hz); MS (ESI) m/z: 251 (M+H$^+$, 100%).

**Methyl 4-benzoxybenzoate (3ah)**

Following general procedure E, the reaction of N-acylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2h (119.1 mg, 0.48 mmol), afforded ketone 3ah$^{8e}$ as a white solid (35.2 mg, 61% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp: 107-108 °C; IR (film): 2920, 2850, 1720, 1647, 1596, 1437, 1399, 1361, 1283, 1194, 1180, 1142, 1109, 1076, 1020, 711, 698 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.15 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 7.9 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 3.97 (s, 3H); $^{13}$C NMR
(125 MHz, CDCl₃): δ 196.1, 166.4, 141.4, 137.0, 133.3, 133.0, 130.2 (2C), 129.9 (2C), 129.6 (2C), 128.6 (2C), 52.6; MS (ESI) m/z 241 (M+H⁺, 100%).

1-(4-Benzoylphenyl)ethanone (3ai)

Following general procedure E, the reaction of N-acetylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2i (111.4 mg, 0.48 mmol), afforded ketone 3ai as a white solid (32.3 mg, 60% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10); mp: 83-84 °C; IR (film): 2917, 1688, 1660, 1597, 1499, 1447, 1403, 1317, 1277, 1180, 1142, 1076, 925, 742, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 2.69 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 197.6, 196.0, 141.4, 139.7, 137.0, 133.1, 130.2 (2C), 130.1 (2C), 128.6 (2C), 128.2 (2C), 26.9; MS (ESI) m/z 247 (M+Na⁺, 100%).

Naphthalen-2-yl(phenyl)methanone (3aj)

Following general procedure E, the reaction of N-acetylpyrrole 1a (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2j (115.2 mg, 0.48 mmol), afforded ketone 3aj as a white solid (45.7 mg, 82% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); mp: 76-77 °C; IR (film): 3058, 2962, 1657, 1598, 1577, 1467, 1446, 1353, 1287, 1235, 1143, 1076, 920, 795, 750, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.26 (s, 1 H), 7.96-7.93 (m, 2H), 7.91 (dd, J = 8.2, 3.6 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.64-7.58 (m, 2H), 7.57-7.48 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.8, 137.0, 134.3, 133.9, 131.5, 131.3, 131.0, 129.2 (2C), 128.5, 127.4 (3C), 127.3, 126.9, 125.9, 124.9; MS (ESI) m/z 255 (M+Na⁺, 100%).

Furan-3-yl(phenyl)methanone (3ak)

Following general procedure E, the reaction of N-acetylpyrrole 1a (41.1 mg, 0.24 mmol) with heteroarylboronic acid neopentyl glycol ester 2k (86.4 mg, 0.48 mmol), afforded ketone 3ak as a light yellow oil (21.1 mg, 51% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); IR (film): 3132, 3060, 1649, 1599, 1577, 1560, 1509, 1446, 1384, 1323, 1195, 1178, 1151, 1079, 1016, 872, 721 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 7.92 (s, 1H), 7.85 (d, 7.8 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.52-7.46 (m, 3H), 6.91 (d, J = 1.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 189.5, 148.6, 144.0, 138.9, 132.5, 128.9 (2C), 128.6 (2C), 126.6, 110.3; MS (ESI) m/z 195 (M+Na⁺, 100%).
(1-Methyl-1H-pyrazol-4-yl)(phenyl)methanone (3a1)

Following general procedure E, the reaction of N-aclypyrrole 1a (41.1 mg, 0.24 mmol) with heteroarylboronic acid neopentyl glycol ester 2l (93.1 mg, 0.48 mmol), afforded ketone 3a1 as a light yellow solid (32.6 mg, 73% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); mp: 81-82 °C; IR (film): 2919, 1642, 1599, 1576, 1542, 1445, 1385, 1238, 1180, 1142, 1076, 893, 726, 713, 670 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.94 (d, J = 4.1 Hz, 2H), 7.84 (dd, J = 8.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 3.98 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 188.9, 141.9, 139.2, 134.3, 132.3, 128.9 (2C), 128.6 (2C), 122.9, 39.5; MS (ESI) m/z 187 (M+H⁺, 100%).

(6-Methoxypyridin-3-yl)(phenyl)methanone (3am)

Following general procedure E (except the T = 80 °C), the reaction of N-aclypyrrole 1a (41.1 mg, 0.24 mmol) with heteroarylboronic acid neopentyl glycol ester 2m (106.1 mg, 0.48 mmol), afforded ketone 3am as a light yellow solid (43.0 mg, 84% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); mp: 59-60 °C; IR (film): 2920, 1655, 1599, 1493, 1446, 1370, 1281, 1196, 1131, 1021, 921, 840, 709 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.62 (dd, J = 2.4, 0.7 Hz, 1H), 8.11 (dd, J = 8.7, 2.5, 1H), 7.80-7.77 (m, 2H), 7.60 (td, J = 7.4, 1.7 Hz, 1H), 7.52-7.47 (m, 2H), 6.84 (dd, J = 8.6 Hz, 0.6 Hz, 1H), 4.03 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 194.3, 166.5, 150.9, 140.1, 137.6, 132.6, 129.8 (2C), 128.5 (2C), 127.0, 111.1, 54.1; MS (ESI) m/z 214 (M+H⁺, 100%).

5. Gram-scale synthesis and a synthetic application

Phenyl(quinolin-6-yl)methanone (3an)

A sealed tube packaged with tin foil paper was charged with powdered K₃PO₄ (2.48 g, 11.68 mmol), N-aclypyrrole 1a (1.00 g, 5.84 mmol), heteroarylboronic acid neopentyl glycol ester 2n (2.11 g, 8.76 mmol), L8-2HCl (393.5 mg, 0.58 mmol) and a magnetic stir bar. Then the sealed tube was taken into a glove box and charged with Ni(COD)₂ (160.7 mg, 0.58 mmol). After that, toluene (11.7 mL) and water (210.2 uL, 11.7 mmol) was added. The sealed tube was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (20 mL),
washed with a saturated aqueous Na₂CO₃ solution (20 mL) and brine (20 mL), and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired ketone 3an as a colorless oil (953.8 mg, 70% Yield). Rf: 0.4 (EtOAc/Hexane = 1/5); IR (film): 3062, 2962, 2929, 1658, 1620, 1597, 1571, 1477, 1458, 1426, 1378, 1327, 1292, 1252, 1185, 1124, 1114, 1076, 861, 845, 801, 770, 718, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.03 (dd, J = 4.2, 1.6 Hz, 1H), 8.29-8.14 (m, 4H), 7.86 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.56-7.46 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 196.1, 152.6, 149.9, 137.5, 137.4, 135.6, 132.8, 131.4, 130.2 (2C), 130.0, 129.6, 128.5 (2C), 127.4, 122.1; HRMS (ESI) m/z calcd for [C₁₆H₁₁NNaO⁺]⁺ (M+Na⁺): 256.0733; found: 256.0729.

Bis(4-fluorophenyl) methanone (3hf)
A sealed tube packed with tin foil paper was charged with powdered K₃PO₄ (2.25 g, 10.58 mmol), N-acylpyrrole 1h (1.00 g, 5.29 mmol), arylboronic acid neopentyl glycol ester 2f (1.65 g, 7.94 mmol), L₈-2HCl (356.4 mg, 0.53 mmol) and a magnetic stir bar. Then the sealed tube was taken into a glove box and charged with Ni(COD)₂ (145.5 mg, 0.53 mmol). After that, toluene (10.6 mL) and water (190.4 µL, 10.58 mmol) was added. The sealed tube was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (20 mL), washed with a saturated aqueous Na₂CO₃ solution (20 mL) and brine (20 mL), and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/20) to yield the desired ketone 7hf as a colorless oil (819.5 mg, 71% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); mp: 107-109 °C; IR (film): 2918, 1649, 1598, 1501, 1409, 1298, 1280, 1229, 1145, 1076, 856, 846, 764 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.85-7.79 (m, 4H), 7.20-7.14 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 193.9, 166.5 (d, J = 254.2 Hz, 2C), 133.8 (d, J = 3.5 Hz, 2C), 132.6 (d, J = 9.2 Hz, 4C), 115.6 (d, J = 21.9 Hz, 4C); MS (ESI) m/z 214 (M+H⁺, 100%).

Quinolin-6-yl(3,4,5-trimethoxyphenyl) methanone (3gn)
A vial packed with tin foil was charged with powdered K₃PO₄ (101.9 mg, 0.48 mmol), N-acylpyrrole 1g (62.7 mg, 0.24 mmol), heteroarylboronic acid neopentyl glycol ester 2n
L8-2HCl (16.2 mg, 0.024 mmol) and a magnetic stir bar. Then the vial was taken into a glove box and charged with Ni(COD)₂ (6.6 mg, 0.024 mmol). After that, toluene (0.5 mL) and water (8.6 μL, 0.48 mmol) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (1 mL), washed with a saturated aqueous Na₂CO₃ solution (1 mL), brine (1 mL) and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/3) to yield the desired ketone 3gn as a light yellow solid (62.1 mg, 80% Yield). Rₜ: 0.5 (EtOAc/Hexane = 1/5); mp: 122-124 °C; IR (film): 2937, 1652, 1619, 1581, 1502, 1460, 1413, 1357, 1332, 1232, 1180, 1127, 1076, 1002, 785, 743 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 9.04 (dd, J = 4.2, 1.8 Hz, 1H), 8.30-8.25 (m, 2H), 8.22 (dd, J = 8.8 Hz, 1H), 8.14 (dd, J = 8.8, 1.9 Hz, 1H), 7.51 (dd, J = 8.4, 4.2 Hz, 1H), 7.12 (s, 2H), 3.97 (s, 3H), 3.88 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 195.1, 153.0 (2C), 152.5, 149.7, 142.4, 137.3, 135.8, 132.4, 130.9, 129.8, 129.5, 127.4, 122.1, 107.9 (2C), 61.0, 56.4 (2C); HRMS (ESI) m/z calcd for [C₁₅H₁₅N⁺NaO₄]⁺ (M+Na⁺): 346.1050; found: 346.1053.

6. Convergent synthesis of diarylketones

General procedure F for synthesis of N-acylpyrroles (1b, 1f) from 1,1'-carbonyldipyrrole 4.

A previously reported procedure was followed.⁷

To a solution of 4 (80.1 mg, 0.50 mmol, 1.0 equiv) in CH₂Cl₂ (4.0 mL, 0.13 M) at −40 °C was added Grignard reagent (1.00 mmol, 2.0 equiv) dropwise. Then the mixture was stirred at −40 °C for 6 h. When complete, the reaction was quenched with saturated aqueous NH₄Cl (4 mL), diluted with EtOAc (4 mL) and warmed to room temperature. The organic layer was washed with saturated aqueous NH₄Cl (2 mL×2), dried over Na₂SO₄, filtered and concentrated. The residue remaining after concentration was dissolved in THF (4.0 mL), cooled to 0 °C, and treated with DBU (4.5 μL, 0.03 mmol). After stirring for 45 min, the reaction was diluted with EtOAc (4 mL), washed with brine (4 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography to yield the desired N-acylpyrrole 1.

(1H-Pyrrol-1-yl)(p-tolyl)methanone (1b)

Following general procedure F, the reaction of 1,1'-carbonyldipyrrole 4 (80.1 mg, 0.5 mmol) with p-tolylmagnesium bromide (1M in 2-MeTHF, 1.0 mL, 1.0 mmol), afforded the desired N-acylpyrrole 1b as a light yellow oil (74.1 mg, 80% Yield). Rₜ: 0.5 (EtOAc/Hexane = 1/20); IR
(4-Methoxyphenyl)(p-tolyl)methanone (3ba)
Following general procedure E, the reaction of N-acylpyrrole 1b (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3ba as a white solid (50.0 mg, 92%). The spectral data are identical with those described above for 3ba.

(4-Methoxyphenyl)(1H-pyrrol-1-yl)methanone (1f)
Following general procedure E, the reaction of 1,1'-carbonyldipyrrrole 4 (80.1 mg, 0.50 mmol) with (4-methoxyphenyl)magnesium bromide (1.0 M in THF, 1.0 mL, 0.50 mmol), afforded the desired N-acylpyrrole 1f as a light yellow oil (81.5 mg, 81% Yield). R: 0.5 (EtOAc/Hexane = 1/20); IR (film): 3147, 2932, 2840, 1690, 1604, 1575, 1512, 1465, 1421, 1400, 1330, 1258, 1172, 1089, 1074, 1027, 883, 843, 764, 742, 645, 623 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.56 (d, J = 8.7 Hz, 2H), 7.29 (t, J = 2.2 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.33 (t, J = 2.2 Hz, 2H), 3.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 167.2, 163.0, 132.1 (2C), 125.3, 121.4 (2C), 113.9 (2C), 112.8 (2C), 55.6; MS (ESI) m/z 224 (M+Na⁺, 100%).

Bis(4-methoxyphenyl)methanone (3fa)
Following general procedure E, the reaction of N-acylpyrrole 1f (48.3 mg, 0.24 mmol) with aryloboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3fa as a pale yellow solid (41.9 mg, 72%). The spectral data are identical with those described above for 3fa.
7. Chemoselective Suzuki-coupling of N-(p-iodo/bromo)benzoylpyrrole with functionalized boronic acids

**Table S6. Reaction optimization**

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<th>Entry</th>
<th>Ni(COD)₂ (x mol%)</th>
<th>L8·2HCl (y mol%)</th>
<th>base (equiv)</th>
<th>Temp, °C</th>
<th>solvent</th>
<th>Yield* of 1sa (%)</th>
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<td>10</td>
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<td>Toluene</td>
<td>15</td>
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<td>2</td>
<td>10</td>
<td>10</td>
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<td>1,4-dioxane</td>
<td>98</td>
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</table>

*Yields were determined by ¹H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. *Isolated yields.

A vial packaged with tin foil was charged with anhydrous base (0.48 mmol, 2.0 equiv), N-(p-iodo)pyrrole 1s (71.3 mg, 0.24 mmol, 1.0 equiv), phenylboronic acid 5a (58.5 mg, 0.48 mmol, 2.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box, charged with Ni(COD)₂ (x mol%) and L8·2HCl (y mol%). After that, solvent (0.5 M) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at T °C for 20 h. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ (1 mL), washed with a saturated aqueous Na₂CO₃ solution (1 mL) and brine (1 mL), and then dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the desired N-acetylpyrrole 1sa.

**General procedure G** for Suzuki-Miyaura coupling of N-(p-iodo/bromobenzoyl)pyrrole 1s/t and arylboronic acids 5a-d to yield N-acetylpyrroles 1sa-1sd.

A vial packaged with tin foil was charged with anhydrous Cs₂CO₃ (156.4 mg, 0.48 mmol, 2.0 equiv), N-(p-iodo/bromobenzoyl)pyrrole 1s/t (71.3 mg, 0.24 mmol, 1.0 equiv), arylboronic acid S (0.48 mmol, 2.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box, charged with Ni(COD)₂ (9.9 mg, 0.036 mmol, 15 mol%) and L8·2HCl (24.3 mg, 0.036 mmol, 15 mol%). After that, 1,4-dioxane (0.5 mL, 0.5 M) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 20 h. After cooling
to room temperature, the mixture was diluted with CH$_2$Cl$_2$ (1 mL), washed with a saturated aqueous Na$_2$CO$_3$ solution (1 mL) and brine (1 mL), and then dried over anhydrous Na$_2$SO$_4$. The combined organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the desired N-acylpyrrole.

(1,1'-Biphenyl-4-yl)(1H-pyrrol-1-yl)methanone (1sa)

Following general procedure G [except Ni(COD)$_2$ (6.6 mg, 0.024 mmol), L8·2HCl (16.2 mg, 0.024 mmol)], the reaction of N-(p-iodo/bromobenzoyl)pyrrole 1s/1t (0.24 mmol) with phenylboronic acid 5a (58.5 mg, 0.48 mmol), afforded the desired N-acylpyrrole 1sa as a white solid (for 1s: 54.6 mg, 92% Yield; for 1t: 49.9 mg, 84% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/20); mp: 109-111 °C; IR (film): 3121, 1681, 1604, 1496, 1404, 1334, 1302, 1192, 1132, 1095, 1076, 882, 851, 741, 704 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.66-7.62 (m, 2H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.41 (t, $J = 7.3$ Hz, 1H), 7.33 (t, $J = 2.1$ Hz, 2H), 6.37 (t, $J = 2.2$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.6, 145.3, 139.8, 131.9, 130.3 (2C), 129.1 (2C), 128.4, 127.3 (2C), 127.2 (2C), 121.4 (2C), 113.2 (2C); HRMS (ESI) $m/z$ calcd for [C$_{17}$H$_{12}$FNNaO]$^+$ (M+Na$^+$): 270.0889; found: 270.0891.

[4'-Fluoro-(1,1'-biphenyl)-4-yl](1H-pyrrol-1-yl)methanone (1sb)

Following general procedure G, the reaction of N-(p-iodobenzoyl)pyrrole 1s (71.3 mg, 0.24 mmol) with arylboronic acid 5b (67.2 mg, 0.48 mmol), afforded the desired N-acylpyrrole 1sb as a white solid (45.8 mg, 72% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/20); mp: 90-92 °C; IR (film): 2922, 1691, 1604, 1523, 1496, 1466, 1399, 1329, 1300, 1256, 1196, 1182, 1159, 1132, 1088, 1075, 882, 828, 741, 716, 632; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 2H), 7.63-7.58 (m, 2H), 7.33 (t, $J = 2.3$ Hz, 2H), 7.37 (t, $J = 2.3$ Hz, 2H), 6.37 (t, $J = 2.3$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.5, 163.1 (d, $J = 248.6$ Hz), 144.3, 135.9 (d, $J = 2.9$ Hz), 132.0, 130.3 (2C), 129.0 (d, $J = 8.2$ Hz, 2C), 127.1 (2C), 121.4 (2C), 116.1 (d, $J = 21.8$ Hz, 2C), 113.3 (2C); HRMS (ESI) $m/z$ calcd for [C$_{17}$H$_{12}$FNNaO]$^+$ (M+Na$^+$): 288.0795; found: 288.0794.

(1H-Pyrrol-1-yl)[4'-(trifluoromethyl)-1,1'-biphenyl-4-yl)methanone (1sc)
Following general procedure G, the reaction of \(N-(p\text{-iodobenzoyl})\text{pyrrole}\ 1s\) (71.3 mg, 0.24 mmol) with arylboronic acid 5c (45.6 mg, 0.48 mmol), affording the desired \(N\text{-acylpyrrole}\ 1sc\) as a white solid (51.5 mg, 68\% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); mp: 132-134 °C; IR (film): 2922, 1684, 1606, 1421, 1397, 1330, 1259, 1161, 1122, 1096, 1073, 1017, 1005, 977, 882, 883, 769, 746, 720, 670; \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 8.2\) Hz, 2H), 7.75 (s, 4H), 7.73 (d, \(J = 8.4\) Hz, 2H), 7.33 (t, \(J = 2.3\) Hz, 2H), 6.38 (t, \(J = 2.3\) Hz, 2H); \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 167.3, 143.7, 143.3, 132.9, 130.5 (q, \(J = 261.0\) Hz), 130.4 (2C), 127.7 (2C), 127.4 (2C), 126.1 (q, \(J = 3.7\) Hz, 2C), 124.2 (q, \(J = 272.4\) Hz), 121.4 (2C), 113.4 (2C); HRMS (ESI) \(m/z\) calcd for [C\(_{18}\)H\(_{12}\)F\(_3\)NNaO\(^+\)] (M+Na\(^+\)): 338.0763; found: 338.0764.

\((1\text{H-Pyrrol-1-yl})\ [(3',4',5'-\text{trimethoxy-}(1,1'-\text{biphenyl})-4-yl)]\text{methanone}\ 1sd\)

Following general procedure G [except Ni(COD)\(_2\) (9.9 mg, 0.036 mmol), L8\cdot2HCl (24.3 mg, 0.036 mmol)], the reaction of \(N-(p\text{-iodobenzoyl})\text{pyrrole}\ 1s\) (71.3 mg, 0.24 mmol) with arylboronic acid 5d (101.8 mg, 0.48 mmol), afforded the desired \(N\text{-acylpyrrole}\ 1sd\) as a white solid (62.4 mg, 77\% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20); mp: 146-148 °C; IR (film): 3145, 2963, 2839, 1090, 1090, 1008, 888, 870, 825, 744, 688; \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 7.9\) Hz, 2H), 7.69 (d, \(J = 8.2\) Hz, 2H), 7.33 (t, \(J = 2.3\) Hz, 2H), 6.83 (s, 2H), 6.37 (t, \(J = 2.4\) Hz, 2H), 3.95 (s, 6H), 3.92 (s, 3H); \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 167.5, 153.8 (2C), 145.4, 138.6, 135.7, 131.9, 130.2 (2C), 127.1 (2C), 121.4 (2C), 113.2 (2C), 104.7 (2C), 61.1, 56.4 (2C); HRMS (ESI) \(m/z\) calcd for [C\(_{20}\)H\(_{19}\)NNaO\(_4\)]\(^+\) (M+Na\(^+\)): 360.1206; found: 360.1205.
8. Sequential C-X and C-N coupling reactions

![Chemical structure]

**[1,1'-Biphenyl]-4-yl(1H-pyrrol-1-yl)methanone (1sa)**

Following **General procedure G**, the reaction of \(N\)-(p-iodobenzoyl)pyrrole 1s (71.3 mg, 0.24 mmol) or \(N\)-(p-bromobenzoyl)pyrrole 1t (60.0 mg, 0.24 mmol) with phenylboronic acid 5a (58.5 mg, 0.48 mmol), afforded the desired \(N\)-acylpyrrole 1sa as a white solid (for 1s: 54.6 mg, 92% Yield; for 1t: 49.9 mg, 84% Yield). Rf: 0.4 (EtOAc/Hexane = 1/20). The spectral data are identical with those described above for 1sa.

**[1,1'-Biphenyl]-4-yl(6-methoxypyridin-3-yl)methanone (6)**

Following **general procedure E** (except \(T = 80^\circ C\)), the reaction of \(N\)-acylpyrrole 1sa (54.6 mg, 0.22 mmol) with heteroarylboronic acid neopentyl glycol ester 2m (97.3 mg, 0.44 mmol), afforded the desired ketone 6 as a white solid (54.9 mg, 79% Yield). Rf: 0.4 (EtOAc/PE = 1/5); mp: 112-113 °C; IR (film): 2921, 1636, 1601, 1558, 1493, 1448, 1403, 1371, 1293, 1264, 1155, 1131, 1017, 853, 835, 738, 698 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.67 (d, \(J = 2.3\) Hz, 1H), 8.12 (d, \(J = 8.7\) Hz, 2H), 7.87 (d, \(J = 8.1\) Hz, 2H), 7.71 (d, \(J = 8.2\) Hz, 2H), 7.65 (d, \(J = 7.7\) Hz, 2H), 7.48 (t, \(J = 7.5\) Hz, 2H), 7.41 (t, \(J = 7.3\) Hz, 1H), 6.86 (d, \(J = 8.6\) Hz, 1H), 4.03 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 193.8, 166.5, 150.7, 145.4, 140.1, 139.9, 136.2, 130.5 (2C), 129.1 (2C), 128.3, 127.4 (2C), 127.2 (2C), 127.1, 111.1, 54.1; HRMS (ESI) \(m/z\) calcd for [C\(_{19}\)H\(_{15}\)NNaO\(_2\)]\(^+\) (M+Na\(^+\)): 312.0995; found 312.0996.
9. The coupling reactions of amides 7–11 with arylboronic acid neopentyl glycol ester 2a

Following general procedure E, the reaction of N-acylindole 7 (53.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3aa as a white solid (48.4 mg, 95% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for 3aa.

Following general procedure E, the reaction of N-acylcarbazole 8 (65.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3aa as a white solid (47.9 mg, 94% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for 3aa.

Following general procedure E, the reaction of N-benzoyl(2,5-dimethyl)pyrrole 9 (47.8 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3aa as a white solid (40.2 mg, 79% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for 3aa.

Following general procedure E, the reaction of N-benzoylindoline 10 (53.6 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3aa as a white solid (12.2 mg, 24% Yield). Rf: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for 3aa.
Following general procedure E, the reaction of \( N,N \)-diphenylbenzamide 11 (65.6 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester 2a (105.6 mg, 0.48 mmol), afforded the desired ketone 3aa as a white solid (7.6 mg, 15% Yield). \( R_f = 0.4 \) (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for 3aa.

References


NMR Spectra

$^1$H and $^{13}$C NMR spectra of compound 13b
$^1$H and $^{13}$C NMR spectra of compound L2·HCl
$^1$H and $^{13}$C NMR spectra of compound L6·2HCl
\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of compound L7·2HCl
$^1$H and $^{13}$C NMR spectra of compound L8·2HCl
$^1$H and $^{13}$C NMR spectra of compound L9·4HBr
$^1$H and $^{13}$C NMR spectra of compound 1c
$^1$H and $^{13}$C NMR spectra of compound 1d
$^1$H and $^{13}$C NMR spectra of compound 1e
$^1$H and $^{13}$C NMR spectra of compound 1g
$^1$H and $^{13}$C NMR spectra of compound 16
$^1$H and $^{13}$C NMR spectra of compound 1k
$^{1}$H and $^{13}$C NMR spectra of compound 19
$^1$H and $^{13}$C NMR spectra of compound 11
\[^1\text{H} \text{ and } ^1\text{C}\text{ NMR spectra of compound 21}\]
$^1$H and $^{13}$C NMR spectra of compound 1m
$^1$H and $^{13}$C NMR spectra of compound 1n
$^{1}$H and $^{13}$C NMR spectra of compound 1o
$^1$H and $^{13}$C NMR spectra of compound 1q
$^1$H and $^{13}$C NMR spectra of compound 1r
$^1$H and $^{13}$C NMR spectra of compound 1s
$^1$H and $^{13}$C NMR spectra of compound 3aa
$^1$H and $^{13}$C NMR spectra of compound 3ba
$^1$H and $^{13}$C NMR spectra of compound 3ca
$^1$H and $^{13}$C NMR spectra of compound 3da
$^1$H and $^{13}$C NMR spectra of compound 3ea
$^1$H and $^{13}$C NMR spectra of compound 3fa
$^1$H and $^{13}$C NMR spectra of compound 3ga
$^1$H and $^{13}$C NMR spectra of compound 3ha
$^1$H and $^{13}$C NMR spectra of compound 3ia
$^1$H and $^{13}$C NMR spectra of compound 3ja
$^1$H and $^{13}$C NMR spectra of compound 3ka
$^1$H and $^{13}$C NMR spectra of compound 3la
$^1$H and $^{13}$C NMR spectra of compound 3ma
$^1$H and $^{13}$C NMR spectra of compound 3na
$^1$H and $^{13}$C NMR spectra of compound 3oa
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound 3pa
$^1$H and $^{13}$C NMR spectra of compound 3qa
$^1$H and $^{13}$C NMR spectra of compound 3ra
$^1$H and $^{13}$C NMR spectra of compound 3ab
$^1$H and $^{13}$C NMR spectra of compound 3ac
$^1$H and $^{13}$C NMR spectra of compound 3ad
$^1$H and $^{13}$C NMR spectra of compound 3ae
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound 3af
$^1$H and $^{13}$C NMR spectra of compound 3ag
$^1$H and $^{13}$C NMR spectra of compound 3ah
$^1$H and $^{13}$C NMR spectra of compound 3ai
$^1$H and $^{13}$C NMR spectra of compound 3aj
$^1$H and $^{13}$C NMR spectra of compound 3ak
$^1$H and $^{13}$C NMR spectra of compound 3al
$^1$H and $^{13}$C NMR spectra of compound 3am
$^1$H and $^{13}$C NMR spectra of compound 3an
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound 3hf
$^1$H and $^{13}$C NMR spectra of compound 3gn
$^1$H and $^{13}$C NMR spectra of compound 6
$^1$H and $^{13}$C NMR spectra of compound 1sa
$^1$H and $^{13}$C NMR spectra of compound 1sb
$^1$H and $^{13}$C NMR spectra of compound 1sc
$^1$H and $^{13}$C NMR spectra of compound 1sd