Electronic Supplementary Information for

Triphenylphosphine-assisted dehydroxylative C\textsuperscript{3}-N bond formation via electrochemical oxidation

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1. General information

Reagents were purchased at the highest commercial quality grade and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (1H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using UV light (254 nm) and TLC stain with anisaldehyde-sulfuric acid for visualization. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). 1H and 13C NMR data were recorded with Bruker (400 MHz) or Jeol (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for 1H), CDCl3 (77.0 ppm for 13C). It is worth to mention that two rotamers of the products were normally observed in 2-substituted N-Boc-pyrrolidine derivatives.¹

2. Experimental procedures

2.1 Electrode materials and dimensions

The instrument for undivided electrolysis is IKA® ElectraSyn 2.0 with carousel. The electrodes used in IKA® ElectraSyn 2.0 were purchased from IKA Company. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) (3.0 cm is the height of the electrode immersed in the solution) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm).

Cyclic voltammograms were recorded on an electrochemical workstation CS150H (CorrTest®). A steady glassy carbon disk electrode (3 mm in diameter) was used as the working electrode; a platinum plate was

used as the counter electrode; the reference was an Ag/AgNO\(_3\) electrode with (0.01 M) AgNO\(_3\) in acetonitrile.

2.2 General procedure for the dehydroxylative Csp\(^3\) – N bond formation

![Chemical structure diagram]

The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm). Azoles or amides (0.3 mmol), "Bu\(_4\)NPF\(_6\) (78 mg, 0.2 mmol), alcohol (0.4 mmol), PPh\(_3\) (105 mg, 0.4 mmol) and MeCN (8 mL) were added to an oven-dried undivided cell (10 mL) equipped with a stirring bar (the order of the addition did not affect the result). The reaction mixture was stirred and electrolyzed at a constant current of 7 mA at room temperature for 3 h. When the reaction was finished, the solvent was evaporated under vacuum and the crude material was purified by column chromatography or preparative TLC to furnish the desired product.

**Table S1. Optimization of the reaction conditions**

<table>
<thead>
<tr>
<th>Entry(^a)</th>
<th>Electrode</th>
<th>Supporting electrolyte</th>
<th>PR(_3)</th>
<th>Yield(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C(+)</td>
<td>Ni(-)</td>
<td>&quot;Bu(_4)NPF(_6)</td>
<td>PPh(_3)</td>
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<tr>
<td>2</td>
<td>C(+)</td>
<td>C(-)</td>
<td>&quot;Bu(_4)NPF(_6)</td>
<td>PPh(_3)</td>
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<tr>
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<td>C(+)</td>
<td>Ni(-)</td>
<td>Et(_4)NPF(_6)</td>
<td>PPh(_3)</td>
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<tr>
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<td>&quot;Bu(_4)NCIO(_4)</td>
<td>PPh(_3)</td>
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<tr>
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<td>Et(_4)NCIO(_4)</td>
<td>PPh(_3)</td>
</tr>
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<tr>
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<td>&quot;Bu(_4)NPF(_6)</td>
<td>&quot;Bu(_3)P</td>
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<tr>
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<td>&quot;Bu(_3)P</td>
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<tr>
<td></td>
<td>C(+)</td>
<td>Ni(-)</td>
<td>&quot;Bu₄NPF₆ Tricyclic ethanol Phosphate</td>
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<tr>
<td>10</td>
<td>C(+)</td>
<td>Ni(-)</td>
<td>&quot;Bu₄NPF₆ Tris(4-fluorophenyl)phosphone</td>
<td>95%</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1a (0.4 mmol), 2a (0.3 mmol), PPh₃ (0.4 mmol), supporting electrolyte (0.025 M), 8 mL MeCN, 23 °C, constant current electrolysis for 3 h, open air. b Isolated yields after chromatography were reported.

Comparing experiments with acids.

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 1H-benzo[d][1,2,3]triazole (36 mg, 0.30 mmol) and C (0.4 mmol) at room temperature for 22 hours. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate or dichloromethane (10 mL x 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound.

<table>
<thead>
<tr>
<th>C</th>
<th>MeCN</th>
<th>DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃·Et₂O</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HOAc</td>
<td>56%</td>
<td>35%</td>
</tr>
<tr>
<td>CF₃CO₂H</td>
<td>64%</td>
<td>65%</td>
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</tbody>
</table>

3. Detail descriptions for products

Tert-butyl 2-(1H-indazol-1-yl)pyrrolidine-1-carboxylate (3a)

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 1H-indazole (36 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL x 3). The crude product was purified
by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 96% yield (83 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 8.01 (s, 1H), 7.80 – 7.45 (m, 2H), 7.41 – 7.31 (m, 1H), 7.13 (t, \(J = 7.5\) Hz, 1H), 6.57 – 6.26 (m, 1H), 3.97 – 3.45 (m, 2H), 2.70 – 1.95 (m, 4H), 1.52 – 1.03 (m, 9H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 154.2, 153.5, 145.1, 139.4, 138.8, 133.5, 126.1, 125.8, 123.5, 120.7, 120.4, 109.8, 109.3, 79.9, 79.7, 69.9, 69.5, 46.5, 33.9, 32.5, 28.1, 27.9, 23.6, 22.6. HRMS m/z (ESI) calcd for C\(_{16}\)H\(_{22}\)N\(_3\)O\(_2\) [(M+H\(^+\)]

Procedure for gram-scale synthesis: The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the nickel plate (3.0 cm × 0.8 cm × 0.2 cm). According to General Procedure, starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (1.5 g, 80 mmol) was reacted with 1H-indazole (720 mg, 60 mmol) and PPh\(_3\) (2.1 g, 80 mmol) were added to an oven-dried undivided cell (10 mL) equipped with a stirring bar. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature for 24 h. Solvent was evaporated under vacuum and the crude material was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 94% yield (1.62 g).

Tert-butyl 2-(4-nitro-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (3b)

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and PPh\(_3\) (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 98% yield (83 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 8.37 – 8.15 (m, 1H), 8.14 – 7.99 (m, 1H), 6.06 – 5.86 (m, 1H), 3.76 – 3.36 (m, 2H), 2.48 – 1.96 (m, 4H), 1.48 – 1.31 (m, 9H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 154.1, 152.9, 135.8, 135.2, 128.3,
127.2, 81.4, 81.1, 74.6, 74.3, 46.9, 46.6, 33.2, 31.7, 28.1, 23.1, 22.0. **HRMS m/z (ESI)** calcd for C$_{12}$H$_{19}$N$_4$O$_4$ ([M+H]$^+$) 283.1401, found 283.1405.

**Tert-butyl 2-(4-nitro-1H-pyrrozol-1-yl)piperidine-1-carboxylate (3c)**

The starting tert-butyl 2-hydroxypiperidine-1-carboxylate (80 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 76% yield (68 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.17 (s, 1H), 8.09 (s, 1H), 6.31 (br s, 1H), 4.14 – 3.97 (m, 1H), 2.99 – 2.88 (m, 1H), 2.60 – 2.55 (m, 1H), 2.02 – 1.91 (m, 1H), 1.80 – 1.56 (m, 4H), 1.48 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 154.6, 135.8, 135.4, 127.6, 81.7, 67.9, 40.1, 28.2, 27.7, 24.0, 18.2. **HRMS m/z (ESI)** calcd for C$_{13}$H$_{21}$N$_4$O$_4$ ([M+H]$^+$) 297.1557, found 297.1562.

**2-(4-nitro-1H-pyrazol-1-yl)cycloheptan-1-ol (3d)**

The starting tert-butyl 2-hydroxyazepane-1-carboxylate (86 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 74% yield (50 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 8.38 – 8.13 (m, 1H), 8.12 – 8.00 (m, 1H), 6.26 – 5.98 (m, 1H), 4.06 – 3.72 (m, 1H), 3.34 – 3.20 (m, 1H), 2.51 – 2.26 (m, 2H), 2.01 – 1.36 (m, 15H). $^{13}$C NMR (100 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 155.5, 154.0, 135.6, 135.2, 128.4, 127.0, 81.7, 81.1, 73.5, 72.0, 42.9, 42.5, 33.4, 32.3, 29.3, 29.1, 29.1, 28.2, 28.2, 23.8, 23.6. **HRMS m/z (ESI)** calcd for C$_{13}$H$_{21}$N$_4$O$_4$ ([M+H]$^+$) 377.1714, found 377.1721.
2-bromo-1-(4-nitro-1H-pyrazol-1-yl)isoindoline (3e)

The starting 2-bromoisoinindolin-1-ol (86 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 78% yield (72 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.2; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 8.44 – 8.16 (m, 1H), 8.11 – 8.00 (m, 1H), 7.51 – 7.27 (m, 4H), 7.15 – 6.98 (m, 1H), 4.94 – 4.77 (m, 2H), 1.55 – 1.38 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture) δ (ppm): 166.6, 150.4, 140.6, 133.4, 131.4, 128.4, 124.9, 123.0, 83.1, 49.1, 28.1. HRMS m/z (ESI) calcd for C₁₆H₁₉N₄O₄ ([M+H]⁺) 331.1401, found 331.1403.

**Tert-butyl (1-(4-nitro-1H-pyrazol-1-yl)hexyl)carbamate (3f)**

The starting tert-butyl (1-hydroxyhexyl)carbamate (87 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 49% yield (46 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.2; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.32 (s, 1H), 8.11 (s, 1H), 5.78 – 5.51 (m, 2H), 2.20 – 1.93 (m, 2H), 1.45 – 1.40 (m, 9H), 1.37 – 1.26 (m, 6H), 0.92 – 0.84 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 174.2, 171.1, 150.1, 82.7, 60.3, 46.4, 32.9, 27.9, 20.9, 17.3, 14.1. HRMS m/z (ESI) calcd for C₁₄H₂₅N₄O₄ ([M+H]⁺) 313.1870, found 313.1872.

4-nitro-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole (3g)
The starting tetrahydro-2H-pyran-2-ol (40.8 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a colorless oil in 51% yield (30 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.34 (s, 1H), 8.07 (s, 1H), 5.44 – 5.35 (m, 1H), 4.12 – 3.66 (m, 2H), 2.22 – 1.60 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 135.4, 126.9, 88.3, 67.7, 30.6, 24.6, 21.5. HRMS m/z (ESI) calcd for C₈H₁₂N₃O₃ ([M+H]⁺) 198.0873, found 198.0870.

The starting tetrahydro-2H-pyran-2-ol (40.8 mg, 0.4 mmol) was reacted with 3,5-diphenyl-1H-pyrazole (66 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a colorless oil in 61% yield (56 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.4; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.92 – 7.86 (m, 1H), 7.61 – 7.56 (m, 1H), 7.52 – 7.27 (m, 6H), 6.65 (s, 1H), 5.26 – 5.20 (m, 1H), 4.21 – 4.14 (m, 1H), 3.68 – 3.59 (m, 1H), 2.76 – 2.64 (m, 1H), 2.15 – 2.05 (m, 1H), 1.92 – 1.59 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.1, 145.5, 133.3, 130.4, 129.0, 128.6, 128.4, 127.7, 125.8, 103.7, 84.4, 67.7, 29.7, 24.8, 22.9. HRMS m/z (ESI) calcd for C₂₀H₂₁N₂O ([M+H]⁺) 305.1648, found 305.1652.
The starting tetrahydro-2H-pyran-2-ol (40.8 mg, 0.4 mmol) was reacted with 1H-indazole (36 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a colorless oil in 60% yield (37 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.15 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.11 – 7.04 (m, 1H), 5.72 – 5.64 (m, 1H), 4.18 – 3.74 (m, 2H), 2.28 – 2.16 (m, 2H), 2.11 – 1.61 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.5, 126.2, 121.8, 121.4, 120.9, 120.5, 117.8, 88.9, 67.9, 31.4, 24.9, 22.1. HRMS m/z (ESI) calcd for C₁₂H₁₅N₂O ([M+H]⁺) 203.1179, found 203.1182.

5-phenyl-2-(tetrahydro-2H-pyran-2-yl)-2H-tetrazole (3j)

The starting tetrahydro-2H-pyran-2-ol (40.8 mg, 0.4 mmol) was reacted with 5-phenyl-2H-tetrazole (44 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound as a colorless oil in 70% yield (48.3 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.2; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.25 – 8.14 (m, 2H), 7.56 – 7.43 (m, 3H), 6.11 – 6.03 (m, 1H), 4.10 – 3.76 (m, 2H), 2.59 – 1.66 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 165.0, 130.3, 128.8, 127.2, 127.0, 87.8, 66.8, 29.0, 24.5, 20.8. HRMS m/z (ESI) calcd for C₁₂H₁₅N₄O ([M+H]⁺) 231.1240, found 231.1245.

2-cinnamyl-5-phenyl-2H-tetrazole (3k)

The starting (E)-3-phenylprop-2-en-1-ol (54 mg, 0.4 mmol) was reacted with 5-phenyl-2H-tetrazole (44 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column

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chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound as a colorless oil in 31% yield (24 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.4; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.20 – 8.12 (m, 2H), 7.50 – 7.32 (m, 8H), 6.62 – 6.52 (m, 2H), 5.52 – 5.29 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 165.1, 136.5, 133.9, 130.2, 128.9, 128.8, 127.5, 126.9, 120.1, 70.0, 29.6, 14.1. HRMS m/z (ESI) calcd for C$_{16}$H$_{15}$N$_4$ ([M+H]$^+$) 263.1291, found 263.1293.

**1-(4-methoxybenzyl)-4-nitro-1H-pyrazole (3l)**

The starting (4-methoxyphenyl)methanol (55 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and tBu$_3$P (89 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a colorless oil in 22% yield (15.3 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.06 (s, 1H), 7.98 (s, 1H), 7.24 (d, $J = 8.3$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 5.22 (s, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 160.1, 135.8, 130.0, 128.0, 125.6, 114.6, 56.8, 55.3. HRMS m/z (ESI) calcd for C$_{11}$H$_{12}$N$_3$O$_3$ ([M+H]$^+$) 234.0873, found 234.0880.

**1-benzhydryl-4-nitro-1H-pyrazole (3m)**

The starting diphenylmethanol (74 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and tBu$_3$P (89 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound as a colorless oil in 24% yield (20 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.2; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.16 (s, 1H), 7.94 (s, 1H), 7.43 – 7.34 (m, 6H), 7.14 – 7.04 (m, 4H), 6.75 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 142.1,
137.5, 132.4, 130.0, 128.2, 127.2, 79.9. **HRMS m/z (ESI)** calcd for C_{16}H_{14}N_{3}O_{2} ([M+H]^+) 280.1081, found 280.1088.

### 4-nitro-1-(2-phenylpropan-2-yl)-1H-pyrazole (3n)

The starting 2-phenylpropan-2-ol (54 mg, 0.4 mmol) was reacted with 4-nitro-1H-pyrazole (34 mg, 0.30 mmol) and iBu_{3}P (89 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL x 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound as a colorless oil in 30% yield (21 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.4; "H NMR (400 MHz, CDCl_{3}) (rotameric mixture) δ (ppm): 8.15 – 8.10 (m, 2H), 7.40 – 7.32 (m, 3H), 7.19 – 7.13 (m, 2H), 2.00 (s, 6H). "C NMR (100 MHz, CDCl_{3}) (rotameric mixture) δ (ppm): 143.7, 135.3, 128.8, 128.1, 127.2, 125.1, 65.6, 29.2. **HRMS m/z (ESI)** calcd for C_{12}H_{14}N_{3}O_{2} ([M+H]^+) 232.1081, found 232.1084.

### Tert-butyl 2-(4-bromo-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (3o)

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 4-bromo-1H-pyrazole (44 mg, 0.30 mmol) and PPh_{3} (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL x 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 83% yield (79 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.2; "H NMR (400 MHz, CDCl_{3}) (rotameric mixture) δ (ppm): 7.76 – 7.38 (m, 2H), 6.05 – 5.82 (m, 1H), 3.76 – 3.29 (m, 2H), 2.51 – 1.88 (m, 4H), 1.58 – 1.26 (m, 9H). "C NMR (100 MHz, CDCl_{3}) (rotameric mixture) δ (ppm): 154.2, 153.3, 139.9, 129.3, 128.0, 92.5, 92.3, 80.8, 80.5, 73.7, 73.2, 46.8, 46.4, 33.4, 31.8, 28.2, 28.1, 23.3, 22.1. **HRMS m/z (ESI)** calcd for C_{12}H_{19}BrN_{3}O_{2} ([M+H]^+) 316.0655, found 316.0659.

510
**Tert-butyl 2-(5-phenyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (3p)**

The starting tert-butyl 2-hydroxyprrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 5-phenyl-1H-pyrazole (44 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound as a colorless oil in 70% yield (66 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 7.89 – 7.77 (m, 2H), 7.68 – 7.43 (m, 1H), 7.43 – 7.34 (m, 2H), 7.33 – 7.26 (m, 1H), 6.51 (s, 1H), 6.11 – 5.93 (m, 1H), 3.81 – 3.39 (m, 2H), 2.63 – 1.94 (m, 4H), 1.55 – 1.32 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture) δ (ppm): 174.3, 150.2, 131.8, 128.7, 128.0, 125.7, 82.7, 46.4, 32.9, 28.0, 17.3. HRMS m/z (ESI) calcd for C₁₈H₂₄N₃O₂ ([M+H]+) 314.1863, found 314.1868.

**Tert-butyl 2-(3,5-diphenyl-1H-pyrazol-1-yl)pyrrolidine-1-carboxylate (3q)**

The starting tert-butyl 2-hydroxyprrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 3,5-diphenyl-1H-pyrazole (66 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound as a white solid in 75% yield (88 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 7.91 – 7.82 (m, 2H), 7.75 – 7.25 (m, 8H), 6.65 – 6.49 (m, 1H), 6.24 – 6.03 (m, 1H), 3.99 – 3.41 (m, 2H), 2.66 – 1.84 (m, 4H), 1.49 – 1.15 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture) δ (ppm): 153.9, 153.5, 150.3, 150.1, 144.6, 144.0, 133.8, 133.6, 130.8, 130.5, 129.3, 128.8, 128.6, 128.4, 128.3, 127.9, 127.4, 127.3, 125.5, 125.4, 103.2, 102.7, 80.0, 79.6, 70.4, 47.2, 47.0, 34.9, 33.6, 28.3, 28.1, 22.9, 22.0. HRMS m/z (ESI) calcd for C₂₄H₂₈N₃O₂ ([M+H]+) 390.2176, found 392.2180.

**Ethyl 1-((tert-butoxycarbonyl)pyrrolidin-2-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate (3r)**
The starting *tert*-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with ethyl 5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (63 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 95% yield (108 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 8.20 – 8.01 (m, 1H), 6.11 – 5.90 (m, 1H), 4.37 – 4.25 (m, 2H), 3.77 – 3.38 (m, 2H), 2.51 – 1.94 (m, 4H), 1.53 – 1.28 (m, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 160.9, 160.8, 154.2, 153.0, 141.6 (q, $J$ = 38.4 Hz), 135.1, 133.9, 120.3 (q, $J$ = 269.2 Hz), 112.3, 81.4, 81.0, 74.6, 74.2, 60.7, 46.9, 46.5, 33.4, 32.0, 28.3, 28.1, 23.1, 21.9, 14.0. HRMS m/z (ESI) calcd for C$_{16}$H$_{23}$F$_3$N$_3$O$_4$ ([M+H]$^+$) 378.1635, found 378.1637.

**Tert-butyl 2-(3-chloro-1*H*-indazol-1-yl)pyrrolidine-1-carboxylate (3s)**

The starting *tert*-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 3-chloro-1*H*-indazole (46 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 70% yield (83 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.4; $^1$H NMR (400 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 7.80 – 7.37 (m, 3H), 7.24 – 7.15 (m, 1H), 6.48 – 6.19 (m, 1H), 3.95 – 3.42 (m, 2H), 2.74 – 1.92 (m, 4H), 1.48 – 1.07 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 154.3, 153.5, 140.9, 140.2, 133.5, 127.4, 127.2, 121.2, 120.7, 119.6, 119.2, 110.5, 109.8, 80.4, 80.1, 70.6, 70.0, 46.8, 46.6, 34.0, 32.6, 28.3, 28.1, 23.7, 22.6. HRMS m/z (ESI) calcd for C$_{16}$H$_{21}$ClN$_3$O$_2$ ([M+H]$^+$) 322.1317, found 322.1323.

**Tert-butyl 2-(4,5-dibromo-2*H*-1,2,3-triazol-2-yl)pyrrolidine-1-carboxylate (3t)**
The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 4,5-dibromo-2H-1,2,3-triazole (68 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 92% yield (109 mg).

RF (petroleum ether/ethyl acetate = 3:1): 0.2; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 6.37 – 6.07 (m, 1H), 3.87 – 3.35 (m, 2H), 2.43 – 1.89 (m, 4H), 1.53 – 1.21 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture, resonances for minor rotamer are marked with m, and resonances for major rotamer are marked with M.) δ (ppm): 153.8m, 153.1M, 124.4m, 124.0M, 81.1M, 81.0m, 77.7m, 77.6M, 46.8m, 46.3M, 33.4M, 32.8m, 28.1m, 28.0M, 22.5m, 21.7M. HRMS m/z (ESI) calcd for C₁₁H₁₇Br₂N₄O₂ ([M+H]+) 396.9692, found 396.9696.

**Tert-butyl 2-(4-nitro-2H-1,2,3-triazol-2-yl)pyrrolidine-1-carboxylate (3u)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 4-nitro-2H-1,2,3-triazole (34 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 83% yield (70 mg).

RF (petroleum ether/ethyl acetate = 5:1): 0.4; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 8.17 (s, 1H), 6.50 – 6.25 (m, 1H), 3.93 – 3.45 (m, 2H), 2.56 – 1.99 (m, 4H), 1.50 – 1.25 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture) δ (ppm): 153.6, 153.1, 153.0, 152.6, 130.3, 130.2, 81.1, 78.4, 46.9, 46.4, 33.6, 32.8, 28.1, 28.0, 22.5, 21.7. HRMS m/z (ESI) calcd for C₁₁H₁₈N₅O₄ ([M+H]+) 284.1353, found 284.1359.

**Tert-butyl 2-([1H-benzo[d][1,2,3]triazol-1-yl]pyrrolidine-1-carboxylate (3v)**
The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 1H-benzo[d][1,2,3]triazole (36 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 85% yield (74 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 8.15 – 7.96 (m, 1H), 7.88 – 7.43 (m, 2H), 7.43 – 7.30 (m, 1H), 6.73 – 6.52 (m, 1H), 4.07 – 3.49 (m, 2H), 2.80 – 2.04 (m, 4H), 1.56 – 1.04 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture, resonances for minor rotamer are marked with m, and resonances for major rotamer are marked with M.) δ (ppm): 154.0⁷m, 153.0⁷M, 145.5⁷(M + M), 132.7ᵐ, 131.7ᵐ, 127.1⁷(m + M), 123.6⁷(m + M), 119.8⁷M, 119.4ᵐ, 110.3ᵐ, 109.6⁷M, 80.7⁷M, 80.4ᵐ, 71.2⁷M, 70.2ᵐ, 46.7ᵐ, 46.6⁷M, 34.3ᵐ, 32.8ᵐ, 28.1ᵐ, 27.8⁷M, 23.5ᵐ, 22.5⁷M. HRMS m/z (ESI) calcd for C₁₅H₂₁N₄O₂ ([M+H]+) 289.1659, found 289.1667.

**Tert-butyl 2-(5-phenyl-2H-tetrazol-2-yl)pyrrolidine-1-carboxylate (3w)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with 5-phenyl-2H-tetrazole (44 mg, 0.30 mmol) and PPh₃ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a white solid in 73% yield (69 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.5; ¹H NMR (400 MHz, CDCl₃) (rotameric mixture) δ (ppm): 8.18 – 8.09 (m, 2H), 7.55 – 7.38 (m, 3H), 6.70 – 6.49 (m, 1H), 3.95 – 3.41 (m, 2H), 2.54 – 1.99 (m, 4H), 1.49 – 1.24 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) (rotameric mixture, resonances for minor rotamer are marked with m, and resonances for major rotamer are marked with M.) δ (ppm): 164.7⁷(m + M), 153.5ᵐ, 152.8⁷M, 130.1ᴹ, 130.0ᵐ, 128.7⁷(m + M), 127.5ᵐ, 127.3ᴹ, 126.7⁷(m + M), 81.1ᴹ, 80.9ᵐ, 75.6ᵐ, 75.3ᴹ, 46.7ᵐ, 46.3ᴹ, 33.5ᴹ, 32.8ᵐ, 28.1ᵐ, 28.0ᴹ, 22.6ᵐ, 21.9ᴹ. HRMS m/z (ESI) calcd for C₁₆H₂₂N₅O₂ ([M+H]+) 316.1768, found 316.1772.

**Tert-butyl 2-(1-oxoisoindolin-2-yl)pyrrolidine-1-carboxylate (3x)**
The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with isoindolin-1-one (40 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 58% yield (53 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.89 – 7.81 (m, 1H), 7.61 – 7.51 (m, 1H), 7.50 – 4.74 (m, 2H), 6.13 (s, 1H), 4.31 (s, 2H), 3.67 – 3.45 (m, 2H), 2.37 – 1.93 (m, 4H), 1.56 – 1.15 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 167.9, 154.1, 140.1, 132.4, 131.4, 128.0, 123.6, 122.7, 80.2, 65.0, 46.5, 45.5, 32.4, 28.1, 23.0. HRMS m/z (ESI) calcd for C$_{17}$H$_{23}$N$_2$O$_3$ ([M+H]$^+$) 303.1703, found 303.1708.

**Tert-butyl 2,5-dioxo-[1,2'-bipyrrolidine]-1'-carboxylate (3y)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with pyrrolidine-2,5-dione (30 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 65% yield (52 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.2; $^1$H NMR (400 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 5.87 – 5.72 (m, 1H), 3.64 – 3.38 (m, 2H), 2.68 – 2.55 (m, 4H), 2.32 – 1.76 (m, 4H), 1.41 – 1.31 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) (rotameric mixture) δ (ppm): 176.5, 175.9, 153.4, 152.9, 80.0, 79.8, 64.6, 64.2, 47.2, 46.9, 31.2, 30.5, 28.4, 28.2, 27.9, 23.9, 23.5. HRMS m/z (ESI) calcd for C$_{13}$H$_{21}$N$_2$O$_4$ ([M+H]$^+$) 269.1496, found 269.1500.

**Tert-butyl 2-(1,3-dioxoisodolin-2-yl)pyrrolidine-1-carboxylate (3z)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with isoidoline-1,3-dione (44 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure.
Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 65% yield (62 mg).

Rf (petroleum ether/ethyl acetate = 1:1): 0.4; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 7.91 – 7.78 (m, 2H), 7.78 – 7.66 (m, 2H), 6.12 – 5.90 (m, 1H), 3.79 – 3.44 (m, 2H), 2.46 – 1.85 (m, 4H), 1.40 – 1.21 (m, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 167.6, 167.3, 153.6, 153.2, 134.1, 133.8, 131.9, 131.8, 123.2, 123.1, 80.1, 79.8, 63.9, 63.6, 47.2, 46.8, 32.0, 31.3, 28.2, 23.9, 23.4. HRMS m/z (ESI) calcd for \(\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_4\) ([M+H]\(^+\)) 317.1496, found 317.1505.

**Tert-butyl 2-(phenylsulphonamido)pyrrolidine-1-carboxylate (3aa)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with benzenesulphonamide (47 mg, 0.30 mmol) and PPh\(_3\) (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the title compound as a white solid in 36% yield (35 mg).

Rf (petroleum ether/ethyl acetate = 1:1): 0.3; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 7.99 – 7.83 (m, 2H), 7.64 – 7.45 (m, 3H), 5.62 – 4.89 (m, 2H), 3.43 – 3.12 (m, 2H), 2.39 – 1.78 (m, 4H), 1.42 – 1.25 (m, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (rotameric mixture) \(\delta\) (ppm): 153.9, 153.3, 141.0, 140.5, 132.4, 128.9, 126.9, 126.6, 80.6, 80.1, 68.0, 45.9, 45.5, 32.9, 31.5, 28.1, 22.5, 21.4. HRMS m/z (ESI) calcd for \(\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_4\text{S}\) ([M+H]\(^+\)) 327.1373, found 327.1380.

**Tert-butyl 2-((N,4-dimethylphenyl)sulphonamido)pyrrolidine-1-carboxylate (3ab)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with \(N\),4-dimethylbenzenesulphonamide (56 mg, 0.30 mmol) and PPh\(_3\) (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3).
The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the title compound as a white solid in 85% yield (90 mg).

Rf (petroleum ether/ethyl acetate = 1:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) (rotameric mixture) $\delta$ (ppm): 7.83 – 7.60 (m, 2H), 7.38 – 7.23 (m, 2H), 5.86 – 5.17 (m, 1H), 3.56 – 3.18 (m, 2H), 2.67 – 2.54 (m, 3H), 2.47 – 2.37 (m, 3H), 2.14 – 1.75 (m, 4H), 1.53 – 1.41 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) (rotameric mixture) $\delta$ (ppm): 152.8, 147.1, 135.4, 129.1, 127.7, 80.1, 78.3, 70.0, 45.7, 33.3, 32.6, 29.0, 28.3, 28.2, 27.8, 22.5, 21.3. HRMS m/z (ESI) calcd for C$_{17}$H$_{27}$N$_2$O$_4$S ([M+H]$^+$) 355.1686, found 355.1693.

**Tert-butyl 2-(2-(phenylsulfonyl)hydrazinyl)pyrrolidine-1-carboxylate (3ac)**

The starting tert-butyl 2-hydroxyprrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with benzenesulfonylhydrazide (52 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 35% yield (36 mg).

Rf (petroleum ether/ethyl acetate = 1:1): 0.4; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.98 – 7.89 (m, 2H), 7.63 – 7.49 (m, 3H), 4.50 – 4.36 (m, 1H), 3.37 – 3.11 (m, 2H), 1.93 – 1.62 (m, 4H), 1.50 – 1.42 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 156.0, 138.2, 132.8, 128.7, 128.1, 80.3, 73.5, 46.7, 29.8, 28.3, 23.1. HRMS m/z (ESI) calcd for C$_{15}$H$_{24}$N$_3$O$_4$S ([M+H]$^+$) 342.1482, found 342.1490.

**Tert-butyl 2-((tert-butoxycarbonyl)amino)pyrrolidine-1-carboxylate (3ad)**

The starting tert-butyl 2-hydroxypyrrolidine-1-carboxylate (75 mg, 0.4 mmol) was reacted with tert-butyl carbamate (35 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a colorless oil in 49% yield (42 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.40 (br s, 1H), 4.78 (br s, 1H), 3.55 – 3.14 (m, 2H), 2.14 – 1.76 (m, 4H), 1.46 (s, 9H), 1.44 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
(ppm): 154.2, 154.1, 79.9, 79.3, 65.6, 45.8, 34.2, 28.4, 28.4, 22.5. HRMS m/z (ESI) calcd for C_{14}H_{27}N_{2}O_{4} ([M+H]^{+}) 287.1965, found 287.1972.

1-((3aS,4S,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-2H-benzo[d][1,2,3]triazole (3ae)

The starting (3aS,4S,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-ol (104 mg, 0.4 mmol) was reacted with 1H-benzo[d][1,2,3]triazole (36 mg, 0.30 mmol) and PPh_{3} (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 75% yield (81 mg). (α:β = 5:1)

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ (ppm): 8.03 – 7.81 (m, 2H), 7.48 – 7.39 (m, 2H), 5.46 (s, 1H), 4.87 – 4.82 (m, 1H), 4.67 (d, J = 6.0 Hz, 1H), 4.49 – 4.43 (m, 1H), 4.29 – 4.24 (m, 1H), 4.14 – 4.07 (m, 2H), 1.46 (s, 6H), 1.39 (s, 3H), 1.31 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ (ppm): 138.7, 125.9, 114.8, 112.5, 109.0, 101.0, 85.4, 79.9, 79.5, 73.2, 66.4, 26.6, 25.6, 25.0, 24.2. HRMS m/z (ESI) calcd for C_{15}H_{21}N_{2}O_{2} ([M+H]^{+}) 362.1710, found 362.1712.

1-((3aS,4S,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1H-indazole (3af)

The starting (3aS,4S,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-ol (105 mg, 0.4 mmol) was reacted with 1H-indazole (36 mg, 0.30 mmol) and PPh\textsubscript{3} (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with
ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 82% yield (89 mg). (α:β = 10:1)

Rf (petroleum ether/ethyl acetate = 3:1): 0.2; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.09 (s, 1H), 7.79 – 7.75 (m, 1H), 7.52 – 7.48 (m, 1H), 7.42 – 7.36 (m, 1H), 7.19 – 7.15 (m, 1H), 5.44 (s, 1H), 4.86 – 4.78 (m, 1H), 4.64 (d, $J$ = 5.9 Hz, 1H), 4.47 – 4.41 (m, 1H), 4.31 – 4.24 (m, 1H), 4.15 – 4.04 (m, 2H), 1.47 (s, 6H), 1.40 (s, 3H), 1.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 139.9, 134.4, 126.8, 123.0, 120.9, 120.8, 112.5, 109.7, 108.9, 101.0, 85.4, 79.9, 79.5, 73.3, 66.3, 26.6, 25.7, 25.1, 24.3. HRMS m/z (ESI) calcd for C$_{16}$H$_{22}$N$_3$O$_2$ ([M+H]$^+$) 361.1758, found 361.1760.

1-((3aS,4S,6aS)-6-(((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-3,5-diphenyl-1H-pyrazole (3ag)

The starting (3aS,4S,6R,6aS)-6-(((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-ol (105 mg, 0.4 mmol) was reacted with 3,5-diphenyl-1H-pyrazole (66 mg, 0.30 mmol) and PPh$_3$ (105 mg, 0.4 mmol) according to General Procedure. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL × 3). The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 90% yield (125 mg). (α:β = 5:1)

Rf (petroleum ether/ethyl acetate = 3:1): 0.2; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.73 – 7.68 (m, 4H), 7.38 – 7.28 (m, 6H), 6.81 (s, 1H), 5.42 (s, 1H), 4.81 – 4.77 (m, 1H), 4.62 (d, $J$ = 5.9 Hz, 1H), 4.44 – 4.38 (m, 1H), 4.25 – 4.21 (m, 1H), 4.10 – 4.00 (m, 2H), 1.46 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 148.7, 131.0, 128.8, 128.2, 125.6, 112.5, 109.0, 101.2, 100.2, 85.4, 80.1, 79.6, 73.2, 66.4, 26.7, 25.7, 25.1, 24.3. HRMS m/z (ESI) calcd for C$_{24}$H$_{28}$N$_3$O$_2$ ([M+H]$^+$) 463.2227, found 463.2226.

4. Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell under air at room temperature. A steady glassy carbon disk electrode (3 mm in diameter) was used as the working electrode; a platinum plate was used as
the counter electrode; the reference was an Ag/AgNO₃ electrode with (0.01 M) AgNO₃ in acetonitrile. 8 mL acetonitrile solvent containing (0.025 M) Bu₄NPF₆ was used as the blank. The spectrums were recorded with the scan rate of 50 mV s⁻¹, from 0 V to 3.0 V (starting from 0 V). The CV of PPh₃, Boc-pyrrolidin-2-ol, and 4-nitro-1H-pyrazole were conducted respectively.

![Graph](image.png)

**Fig 1.** Cyclic voltammograms recorded in (0.025 M) Bu₄NPF₆-MeCN solution: scan rate: 50 mV s⁻¹; starting potential: 0 V; glass carbon (3 mm diameter, Working Electrode); platinum plate (Counter Electrode); Ag/AgNO₃ (0.01 M) AgNO₃ in MeCN (Reference Electrode); Concentrations: PPh₃ (0.2 mmol / 8 ml MeCN), Boc-pyrrolidin-2-ol (0.2 mmol / 8 ml MeCN), 4-nitro-1H-pyrazole (0.15 mmol / 8 ml MeCN)
5. $^1$H and $^{13}$C NMR spectra

3a (rotameric mixture)
3b (rotameric mixture)
3d (rotameric mixture)
3e (rotameric mixture)
3o (rotameric mixture)
3q (rotameric mixture)
3r (rotameric mixture)
3s (rotameric mixture)
3u (rotameric mixture)
3v (rotameric mixture)
3w (rotameric mixture)
3y (rotameric mixture)
3z (rotameric mixture)
3aa (rotameric mixture)
3ab (rotameric mixture)
3ac (rotameric mixture)
3ae (anomeric mixtures α:β = 5:1)
3af (anomeric mixtures $\alpha:\beta = 10:1$)
3ag (anomeric mixtures α:β = 5:1)