Electronic Supplementary Information

Direct N-acylation of azoles via metal-free catalyzed oxidative cross-coupling strategy

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**General Information:**

All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 300–400 meshes. The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III spectrometer and are referenced to the residual solvent signals (7.26 ppm for $^1$H and 77.0 ppm for $^{13}$C in CDCl$_3$). The HRMS spectra were recorded on a Bruker micrOTOF Q II spectrometer.

**General Procedure for $N$-Acylation of Azoles (3, 5):**

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of azole, 4, 0.45 mmol of aldehyde or benzil (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over MgSO$_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product 3, 5.

To a 100 mL round-bottom flask with a stir bar was added 20 mmol of benzoimidazole, 30 mmol of benzaldehyde (1.5 equiv), followed by 4 mmol of KI (0.2 equiv). Then 25 mL of DCE was added, followed by 60 mmol of TBHP (70% aqueous). The flask with a condenser was open in air. The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over MgSO$_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product 5a (3.78 g, 85% yield).
General Procedure for Radical Trapping Experiments:

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1H-pyrazole 1a, 0.45 mmol of 3,4-dimethoxybenzaldehyde 2a (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous) and 0.9 mmol of TEMPO (2,2,6,6-Tetramethylpiperidinooxy). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over MgSO₄, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford 6 in 99% yield.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1H-pyrazole 1a, 0.45 mmol of 3,4-dimethoxybenzaldehyde 2a (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous) and 0.9 mmol of 1,1-Diphenylethylene. The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. Only trace 3a was detected by GC-MS.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1H-pyrazole 1a, 0.45 mmol of benzil (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous) and 0.9 mmol of TEMPO. The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The desired product was not detected by GC-MS.
General Procedure for Control Experiments:

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of pyrazole 1a, 0.45 mmol of aliphatic aldehyde (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The desired product was not detected by GC-MS. The pyrazole 1a and corresponding aliphatic aldehyde were recovered, unusual product was not detected by GC-MS.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3-phenylpropanal, 0.9 mmol of TEMPO, followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The corresponding aliphatic aldehyde was recovered, and the coupling product of 3-phenylpropanal and TEMPO was not detected by GC-MS.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of benzaldehyde, 0.36 mmol of butan-1-amine (1.2 equiv), followed by 0.015 mmol of KI (0.05 equiv). Then 3 mL of H₂O was added, followed by 0.66 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 15 h, cooled to room temperature. The amide was detected as the major product by GC-MS.
To a 15 mL pressure tube with a stir bar was added 0.3 mmol of benzaldehyde, 0.36 mmol of butan-1-amine (1.2 equiv), followed by 0.015 mmol of KI (0.05 equiv) and 0.66 mmol of TEMPO (2.2 equiv). Then 3 mL of H$_2$O was added, followed by 0.66 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 °C for 15 h, cooled to room temperature. The amide and the coupling product of acyl radical and TEMPO were not detected by GC-MS. Instead, the imine product was observed as the major product by GC-MS.

\[
\text{C}_6\text{H}_5\text{O}^+ + \text{CH}_3\text{CN, 80 °C, 5 h} \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N}
\]

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 4-chlorobenzaldehyde, 0.36 mmol of morpholine (1.2 equiv). Then 3 mL of CH$_3$CN was added, followed by 0.36 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 °C for 5 h, cooled to room temperature. The amide was detected as the major product by GC-MS.

\[
\text{Cl}-\text{C}_6\text{H}_5\text{O}^+ + \text{CH}_3\text{CN, 80 °C, 5 h} \rightarrow \text{Cl}-\text{C}_6\text{H}_5\text{C}=\text{N}
\]

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 4-chlorobenzaldehyde, 0.36 mmol of morpholine (1.2 equiv), followed by 0.66 mmol of TEMPO (2.2 equiv). Then 3 mL of CH$_3$CN was added, followed by 0.36 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 °C for 5 h, cooled to room temperature. Only trace amide was detected by GC-MS. And the coupling product of acyl radical and TEMPO were not detected by GC-MS.

\[
\text{Cl}-\text{C}_6\text{H}_5\text{O}^+ + \text{CH}_3\text{CN, 80 °C, 5 h} \rightarrow \text{Cl}-\text{C}_6\text{H}_5\text{C}=\text{N}
\]

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3,4-dimethoxybenzaldehyde 2a, 0.36 mmol of 3-phenyl-1H-pyrazole 1a (1.2 equiv), followed by 0.015 mmol of KI (0.05 equiv). Then 3 mL of H$_2$O was added, followed by 0.66 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 °C for 15 h, cooled to room temperature. Only trace 3a was detected by GC-MS.
To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3,4-dimethoxybenzaldehyde 2a, 0.36 mmol of 3-phenyl-1H-pyrazole 1a (1.2 equiv). Then 3 mL of CH$_3$CN was added, followed by 0.36 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 °C for 5 h, cooled to room temperature. Only trace 3a was detected by GC-MS.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1H-pyrazole 1a, followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 °C for 12 h, cooled to room temperature. The coupling product of 1a and TEMPO was not detected by GC-MS.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1H-pyrazole 1a, followed by 0.3 mmol of I$_2$ or NIS (1 equiv). Then 3 mL of DCE was added. The reaction mixture was stirred at room temperature for 12 h. The 1-iodo-3-phenyl-1H-pyrazole was not detected by GC-MS.
Characterization Data of Compounds 3a-3p:

(3,4-dimethoxyphenyl)(5-phenyl-1H-pyrazol-1-yl)methanone  (3a)  [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 2.9$ Hz, 1 H), 8.14 (dd, $J = 8.5$, 2.1 Hz, 1 H), 7.96 (d, $J = 2.0$ Hz, 1 H), 7.93–7.87 (m, 2 H), 7.50–7.36 (m, 3 H), 6.99 (t, $J = 8.2$ Hz, 1 H), 6.85 (d, $J = 2.9$ Hz, 1 H), 4.00 (s, 3 H), 3.98 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.9, 155.6, 153.4, 148.3, 132.0, 132.0, 129.1, 128.8, 127.2, 126.3, 123.5, 114.7, 110.1, 106.7, 56.1, 56.0; HRMS (ESI) Calcd for C$_{18}$H$_{16}$N$_2$NaO$_3$ [M+Na]$^+$ 331.1066, Found 331.1053.

Phenyl(5-phenyl-1H-pyrazol-1-yl)methanone  (3b) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 2.9$ Hz, 1 H), 8.31–8.25 (m, 2 H), 7.93–7.87 (m, 2 H), 7.68–7.62 (m, 1 H), 7.58–7.51 (m, 2 H), 7.47–7.37 (m, 3 H), 6.87 (d, $J = 2.9$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 155.9, 133.0, 131.9, 131.8, 131.7, 131.5, 129.2, 128.7, 128.0, 126.4, 107.2; HRMS (ESI) Calcd for C$_{16}$H$_{12}$N$_2$NaO [M+Na]$^+$ 271.0844, Found 271.0842.

(4-methoxyphenyl)(5-phenyl-1H-pyrazol-1-yl)methanone  (3c) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (t, $J = 3.6$ Hz, 1 H), 8.42–8.35 (m, 2 H), 7.92–7.89 (m, 2 H), 7.50–7.37 (m, 3 H), 7.05–6.99 (m, 2 H), 6.84 (d, $J = 2.9$ Hz, 1 H), 3.91 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.1, 163.6, 155.5, 134.5, 132.0, 131.8, 129.0, 128.7, 126.3, 123.5, 113.4, 106.7, 55.5; HRMS (ESI) Calcd for C$_{17}$H$_{14}$N$_2$NaO$_2$ [M+Na]$^+$ 301.0962, Found 301.0947.
(4-(tert-butyl)phenyl)(5-phenyl-1H-pyrazol-1-yl)methanone  (3d) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 2.9$ Hz, 1 H), 8.31 – 8.22 (m, 2 H), 7.96 – 7.88 (m, 2 H), 7.61 – 7.54 (m, 2 H), 7.50 – 7.37 (m, 3 H), 6.86 (d, $J = 2.9$ Hz, 1 H), 1.40 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.8, 156.8, 155.7, 132.0, 131.9, 131.7, 129.1, 128.7, 128.5, 126.4, 125.1, 106.9, 35.1, 31.1; HRMS (ESI) Calcd for C$\text{_{20}}$H$\text{_{20}}$N$_2$NaO [M+Na]$^{+}$ 327.1460, Found 327.1468.

(4-bromophenyl)(5-phenyl-1H-pyrazol-1-yl)methanone  (3e) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (s, 1 H), 8.18–8.13 (m, 1 H), 7.85–7.83 (m, 1 H), 7.78–7.72 (m, 2 H), 7.68 (dd, $J = 8.6$, 1.9 Hz, 2 H), 7.51–7.39 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 144.1, 142.6, 132.4, 132.0, 131.6, 131.0, 128.4, 125.9, 125.4, 120.7, 115.4; HRMS (ESI) Calcd for C$_{14}$H$_9$BrN$_2$NaO [M+Na]$^{+}$ 322.9782, Found 322.9790.

(4-chlorophenyl)(5-phenyl-1H-pyrazol-1-yl)methanone  (3f) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 2.9$ Hz, 1 H), 8.31–8.23 (m, 2 H), 7.93–7.84 (m, 2 H), 7.54–7.50 (m, 2 H), 7.48–7.38 (m, 3 H), 6.88 (d, $J = 2.9$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 156.1, 139.6, 133.4, 131.7, 131.6, 129.8, 129.3, 128.8, 128.4, 126.4, 107.4; HRMS (ESI) Calcd for C$_{16}$H$_{11}$ClN$_2$NaO [M+Na]$^{+}$ 305.0448, Found 305.0452.
4-(5-phenyl-1H-pyrazole-1-carbonyl)benzonitrile (3g) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.48 (d, $J = 2.9$ Hz, 1 H), 8.34 (d, $J = 8.2$ Hz, 2 H), 7.90–7.79 (m, 4 H), 7.48–7.40 (m, 3 H), 6.91 (d, $J = 2.9$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.5, 156.6, 135.4, 132.1, 131.7, 131.6, 131.2, 129.5, 128.8, 126.4, 117.9, 116.1, 108.0; HRMS (ESI) Calcd for C$_{17}$H$_{11}$N$_3$NaO [M+Na] 296.0794, Found 296.0794.

(2-methoxyphenyl)(5-phenyl-1H-pyrazol-1-yl)methanone (3h) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29 (d, $J = 2.9$ Hz, 1 H), 7.86–7.78 (m, 2 H), 7.59–7.50 (m, 2 H), 7.42–7.35 (m, 3 H), 7.09–7.03 (m, 2 H), 6.81 (d, $J = 2.9$ Hz, 1 H), 3.82 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.5, 157.9, 155.7, 132.7, 131.9, 131.1, 130.5, 129.1, 128.6, 126.4, 122.7, 120.2, 111.6, 107.3, 55.9; HRMS (ESI) Calcd for C$_{17}$H$_{14}$N$_2$NaO$_2$ [M+Na] 301.0954, Found 301.0947.

(3-fluorophenyl)(5-phenyl-1H-pyrazol-1-yl)methanone (3i) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.48 (d, $J = 2.9$ Hz, 1 H), 8.11–8.07 (m, 1 H), 8.07–8.02 (m, 1 H), 7.92–7.86 (m, 2 H), 7.51 (td, $J = 8.0$, 5.6 Hz, 1 H), 7.48–7.38 (m, 3 H), 7.35 (td, $J = 8.3$, 2.6, 0.9 Hz, 1 H), 6.89 (d, $J = 2.9$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.7, 162.1 ($^1$J$_{CF} = 246.8$ Hz), 156.3, 133.4 ($^1$J$_{CF} = 7.8$ Hz), 131.8, 131.6, 129.7 ($^1$J$_{CF} = 7.8$ Hz), 129.4, 128.8, 127.7 ($^1$J$_{CF} = 3.2$ Hz), 126.4, 120.1
(3,5-dimethoxyphenyl)(5-phenyl-1H-pyrazol-1-yl)methanone (3j)

[New compound].

\[ \text{1H} \text{ NMR (400 MHz, CDCl}_3\delta \text{ 8.46 (d, } J = 2.9 \text{ Hz, 1 H), 7.93–7.85 (m, 2 H), 7.46–7.39 (m, 5 H), 6.87 (d, } J = 2.9 \text{ Hz, 1 H), 6.73 (t, } J = 2.3 \text{ Hz, 1 H), 3.87 (s, 6 H); } \text{13C} \text{ NMR (100 MHz, CDCl}_3\delta \text{ 165.7, 160.2, 155.9, 133.0, 132.0, 131.8, 129.2, 128.8, 126.3, 109.6, 107.2, 105.9, 55.6; HRMS (ESI) Calcd for C}_{18}H_{16}N_{2}O_3 [M+Na] 331.1054, Found 331.1053.]

naphthalen-2-yl(5-phenyl-1H-pyrazol-1-yl)methanone (3k) [New compound].

\[ \text{1H} \text{ NMR (400 MHz, CDCl}_3\delta \text{ 8.93 (s, 1 H), 8.54 (d, } J = 2.9 \text{ Hz, 1 H), 8.31–8.24 (m, 1 H), 8.03 (d, } J = 8.1 \text{ Hz, 1 H), 7.97 (d, } J = 8.7 \text{ Hz, 1 H), 7.94–7.91 (m, 3 H), 7.67–7.63 (m, 1 H), 7.61–7.57 (m, 1 H), 7.50–7.37 (m, 3 H), 6.90 (d, } J = 2.9 \text{ Hz, 1 H); } \text{13C} \text{ NMR (100 MHz, CDCl}_3\delta \text{ 166.1, 155.9, 135.4, 134.1, 132.2, 131.8, 129.7, 129.2, 128.8, 128.6, 127.7, 127.6, 127.5, 126.7, 126.4, 107.1; HRMS (ESI) Calcd for C}_{20}H_{14}N_{2}O [M+Na] 321.1000, Found 321.0998.]

(5-phenyl-1H-pyrazol-1-yl)(thiophen-2-yl)methanone (3l) [New compound].

\[ \text{1H} \text{ NMR (400 MHz, CDCl}_3\delta \text{ 8.48 (dd, } J = 3.9, 1.3 \text{ Hz, 1 H), 8.46 (d, } J = 2.9 \text{ Hz, 1 H), 7.98 (dd, } J = 5.3, 1.3 \text{ Hz, 1 H).}]

3.3 Hz, 2 H), 7.84 (dd, J = 5.0, 1.3 Hz, 1 H), 7.53–7.46 (m, 2 H), 7.43 (ddd, J = 7.4, 3.7, 1.3 Hz, 1 H), 7.22 (dd, J = 4.9, 4.0 Hz, 1 H), 6.86 (d, J = 2.9 Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.6, 155.5, 138.5, 137.7, 132.2, 131.7, 130.8, 129.2, 128.8, 127.2, 126.4, 107.3; HRMS (ESI) Calcd for C\(_{14}\)H\(_{10}\)N\(_2\)NaOS [M+Na] 277.0398, Found 277.0406.

![3m](image)

**3m (4-bromophenyl)(3-methyl-1\(H\)-pyrazol-1-yl)methanone (3m) [New compound].** \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, J = 2.7 Hz, 1 H), 8.08–7.99 (m, 2 H), 7.67–7.61 (m, 2 H), 6.34 (d, J = 2.8 Hz, 1 H), 2.35 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.1, 154.7, 133.1, 131.4, 131.1, 130.5, 128.1, 110.5, 14.0; HRMS (ESI) Calcd for C\(_{11}\)H\(_9\)BrN\(_2\)NaO [M+Na] 286.9786, Found 286.9790.

![3n](image)

**3n (4-bromophenyl)(1\(H\)-pyrazol-1-yl)methanone (3n) [New compound].** \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43 (dd, J = 2.9, 0.5 Hz, 1 H), 8.08–7.99 (m, 2 H), 7.80 (d, J = 0.7 Hz, 1 H), 7.71–7.62 (m, 2 H), 6.53 (dd, J = 2.8, 1.5 Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.4, 144.7, 133.1, 131.4, 130.4, 130.2, 128.3, 109.7; HRMS (ESI) Calcd for C\(_{10}\)H\(_7\)BrN\(_2\)NaO [M+Na] 272.9639, Found 272.9634.

![5a](image)

**5a (1\(H\)-benzo[d]imidazol-1-yl)(phenyl)methanone (5a)**. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.22 (s, 1 H), 8.22–8.19 (m, 1 H), 7.87–7.83 (m, 1 H), 7.81 (dd, J = 5.2, 3.3 Hz, 2 H), 7.74–7.67 (m, 1 H), 7.62–7.58 (m, 2 H), 7.49–7.41 (m, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.1, 144.1, 143.1, 133.2, 132.9, 132.1, 129.5, 129.1, 125.8, 125.3, 120.6, 115.5; HRMS (ESI) Calcd for C\(_{13}\)H\(_{10}\)N\(_2\)O [M+H] 223.0866, Found 223.0866.
(1H-benzo[d]imidazol-1-yl)(4-bromophenyl)methanone (5b) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 1 H), 8.18–8.13 (m, 1 H), 7.85–7.83 (m, 1 H), 7.78–7.72 (m, 2 H), 7.68 (dd, $J$ = 8.6, 1.9 Hz, 2 H), 7.51–7.39 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.1, 144.1, 142.6, 132.4, 132.0, 131.6, 131.0, 128.4, 125.9, 125.4, 120.7, 115.4; HRMS (ESI) Calcd for C$_{14}$H$_9$BrN$_2$O [M+Na] 322.9782, Found 322.9790.

4-(1H-benzo[d]imidazole-1-carbonyl)benzonitrile (5c) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21–8.14 (m, 1 H), 8.12 (s, 1 H), 7.97–7.88 (m, 4 H), 7.87–7.82 (m, 1 H), 7.51–7.43 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.3, 144.1, 142.3, 136.7, 132.9, 131.8, 129.9, 126.3, 125.9, 120.9, 117.4, 116.8, 115.5; HRMS (ESI) Calcd for C$_{15}$H$_9$N$_3$O [M+Na] 270.0630, Found 270.0638.

(1H-benzo[d]imidazol-1-yl)(2-methoxyphenyl)methanone (5d) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.30–8.21 (m, 1 H), 7.97 (s, 1 H), 7.86–7.73 (m, 1 H), 7.59 (m, 1 H), 7.54 (dd, $J$ = 7.6, 1.6 Hz, 1 H), 7.48–7.37 (m, 2 H), 7.14 (td, $J$ = 7.5, 0.8 Hz, 1 H), 7.06 (d, $J$ = 8.4 Hz, 1 H), 3.78 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 156.5, 144.1, 143.6, 133.5, 131.6, 129.9, 125.7, 125.1, 122.9, 121.2, 120.3, 115.5, 111.6, 55.7; HRMS (ESI) Calcd for C$_{15}$H$_{12}$N$_2$O$_2$ [M+Na] 275.0794, Found 275.0791.
(1H-benzo[d]imidazol-1-yl)(2-bromophenyl)methanone (5e) [New compound]. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.20 (d, \(J = 5.4\) Hz, 1 H), 7.90 (s, 1 H), 7.87–7.81 (m, 1 H), 7.76–7.74 (m, 1 H), 7.60–7.39 (m, 5 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 165.2, 144.2, 142.7, 135.3, 133.5, 132.6, 131.3, 129.2, 127.9, 126.029, 125.5, 120.6, 119.7, 115.4; HRMS (ESI) Calcd for C\textsubscript{14}H\textsubscript{9}BrN\textsubscript{2}NaO \([\text{M+Na}]\) 322.9793, Found 322.9790.

(1H-benzo[d]imidazol-1-yl)(3,4-dimethoxyphenyl)methanone (5f) [New compound]. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.31 (s, 1 H), 8.17–8.09 (m, 1 H), 7.89–7.80 (m, 1 H), 7.48–7.38 (m, 4 H), 7.06–6.95 (m, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.4, 153.5, 149.4, 144.0, 143.1, 132.3, 125.5, 125.0, 124.8, 124.1, 120.4, 115.2, 112.3, 110.4, 56.2, 56.1; HRMS (ESI) Calcd for C\textsubscript{16}H\textsubscript{14}N\textsubscript{2}NaO \([\text{M+Na}]\) 305.0902, Found 305.0897.

(1H-benzo[d]imidazol-1-yl)(3-nitrophenyl)methanone (5g) [New compound]. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.69 (t, \(J = 1.9\) Hz, 1 H), 8.56 (ddd, \(J = 8.3, 2.2, 1.0\) Hz, 1 H), 8.23–8.17 (m, 1 H), 8.16 (s, 1 H), 8.16–8.12 (m, 1 H), 7.91–7.81 (m, 2 H), 7.54–7.44 (m, 2 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 164.6, 148.4, 144.1, 142.1, 134.8, 134.5, 131.8, 130.5, 127.6, 126.3, 125.9, 124.5, 120.9, 115.5; HRMS (ESI) Calcd for C\textsubscript{14}H\textsubscript{10}N\textsubscript{3}O\textsubscript{3} \([\text{M+H}]\) 268.0712, Found 268.0717.
(1H-benzo[d]imidazol-1-yl)(naphthalen-2-yl)methanone (5h) [New compound]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (s, 2 H), 8.26–8.19 (m, 1 H), 8.04 (d, \(J = 8.5\) Hz, 1 H), 7.96 (d, \(J = 8.7\) Hz, 2 H), 7.90–7.83 (m, 2 H), 7.72–7.66 (m, 1 H), 7.65–7.60 (m, 1 H), 7.50–7.42 (m, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.1, 144.1, 143.2, 135.3, 132.2, 131.1, 129.9, 129.2, 129.0, 128.0, 127.5, 125.7, 125.2, 125.0, 120.6, 115.4; HRMS (ESI) Calcd for C\(_{18}\)H\(_{12}\)N\(_2\)O \([\text{M+Na}]^+\) 295.0849, Found 295.0842.

\[ \text{\includegraphics[width=0.2\textwidth]{5h.png}} \]

(1H-benzo[d]imidazol-1-yl)(thiophen-2-yl)methanone (5i) [New compound]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.54 (s, 1 H), 8.23–8.14 (m, 1 H), 7.88–7.80 (m, 2 H), 7.81–7.76 (m, 1 H), 7.50–7.39 (m, 2 H), 7.28–7.26 (m, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.9, 143.9, 142.2, 135.7, 134.5, 134.3, 132.2, 128.2, 125.7, 125.2, 120.5, 115.3; HRMS (ESI) Calcd for C\(_{12}\)H\(_9\)N\(_2\)OS \([\text{M+H}]^+\) 229.0431, Found 229.0430.

\[ \text{\includegraphics[width=0.2\textwidth]{5i.png}} \]

(1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (5j). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.40 (d, \(J = 8.3\) Hz, 1 H), 8.25–8.19 (m, 2 H), 8.17 (d, \(J = 8.3\) Hz, 1 H), 7.74–7.67 (m, 2 H), 7.62–7.52 (m, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.7, 145.7, 133.7, 132.3, 131.7, 131.5, 130.4, 128.4, 126.3, 120.2, 114.8; HRMS (ESI) Calcd for C\(_{13}\)H\(_9\)N\(_3\)O \([\text{M+Na}]^+\) 246.0630, Found 246.0638.

\[ \text{\includegraphics[width=0.2\textwidth]{5j.png}} \]

1H-benzo[d][1,2,3]triazol-1-yl)(2-bromophenyl)methanone (5m) [New compound]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.41 (dd, \(J = 8.3, 0.7\) Hz, 1 H), 8.16 (dd, \(J = 8.3, 0.7\) Hz, 1 H), 7.77–7.70 (m, 2 H), 7.64–7.60 (m, 1 H), 7.60–7.54 (m, 1 H), 7.53–7.44 (m, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.6, 145.7, 133.7, 132.3, 131.7, 131.5, 130.4, 128.4, 126.3, 120.2, 114.8; HRMS (ESI) Calcd for C\(_{13}\)H\(_9\)N\(_3\)O \([\text{M+Na}]^+\) 246.0630, Found 246.0638.
MHz, CDCl$_3$) $\delta$ 166.4, 146.2, 135.0, 133.2, 132.5, 131.3, 130.7, 130.1, 127.2, 126.7, 120.6, 120.4, 114.4; HRMS (ESI) Calcd for C$_{13}$H$_8$BrN$_3$O$_2$ [M+Na] 323.9736, Found 323.9743.

(1H-benzo[d][1,2,3]triazol-1-yl)(2-methoxyphenyl)methanone (5n) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (d, $J$ = 8.3 Hz, 1 H), 8.13 (d, $J$ = 8.3 Hz, 1 H), 7.69 (ddd, $J$ = 8.2, 7.2, 1.0 Hz, 1 H), 7.63–7.50 (m, 3 H), 7.12 (td, $J$ = 7.5, 0.8 Hz, 1 H), 7.06 (d, $J$ = 8.4 Hz, 1 H), 3.77 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.9, 157.8, 146.0, 135.3, 131.4, 130.3, 130.2, 126.1, 122.7, 120.5, 120.1, 114.4, 111.7, 55.8; HRMS (ESI) Calcd for C$_{14}$H$_{11}$N$_3$O$_2$ [M+Na] 276.0738, Found 276.0743.

(4-bromophenyl)(1H-indazol-1-yl)methanone (5o) [New compound]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (dd, $J$ = 8.4, 0.7 Hz, 1 H), 8.21 (d, $J$ = 0.6 Hz, 1 H), 8.01–7.93 (m, 2 H), 7.83–7.76 (m, 1 H), 7.68–7.65 (m, 2 H), 7.64–7.61 (m, 1 H), 7.48–7.39 (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 140.6, 140.1, 132.6, 132.1, 131.3, 129.7, 127.3, 126.1, 125.0, 121.0, 115.9; HRMS (ESI) Calcd for C$_{14}$H$_9$BrN$_2$O$_2$ [M+Na] 322.9789, Found 322.9790.

2,2,6,6-tetramethylpiperidin-1-yl 3,4-dimethoxybenzoate (6). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (dd, $J$ = 8.4, 1.5 Hz, 1 H), 7.54 (d, $J$ = 1.5 Hz, 1 H), 6.86 (d, $J$ = 8.4 Hz, 1 H), 3.89 (s, 6 H), 1.76–1.39 (m, 6 H), 1.22 (s, 6 H), 1.07 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.0, 152.7, 148.6, 123.0, 121.9, 112.1, 110.1, 60.1, 55.8, 55.77, 38.8, 31.8, 20.6, 16.8; HRMS (ESI) Calcd for C$_{18}$H$_{27}$NNaO$_4$ [M+Na] 344.1825, Found 344.1832.
References:


Copies of $^1$H and $^{13}$C NMR Spectra

$^1$H NMR of product 3a

$^{13}$C NMR of product 3a
$^1$H NMR of product 3b

$^{13}$C NMR of product 3b
$^1$H NMR of product 3c

$^{13}$C NMR of product 3c
$^1$H NMR of product 3d

$^{13}$C NMR of product 3d
$^1$H NMR of product 3e

$^{13}$C NMR of product 3e
\( ^1H \text{ NMR of product } 3f \)

\( ^{13}C \text{ NMR of product } 3f \)
$^1$H NMR of product 3g

$^{13}$C NMR of product 3g
$^1$H NMR of product 3h

$^{13}$C NMR of product 3h
$^1$H NMR of product 3i

$^{13}$C NMR of product 3i
$^1$H NMR of product 3j

$^{13}$C NMR of product 3j
$^1$H NMR of product 3k

$^{13}$C NMR of product 3k
$^1$H NMR of product 3l

$^{13}$C NMR of product 3l
$^1$H NMR of product 3m

$^{13}$C NMR of product 3m
$^1$H NMR of product 3n

$^{13}$C NMR of product 3n
$^1$H NMR of product 5a

$^{13}$C NMR of product 5a
$^1$H NMR of product 5b

$^{13}$C NMR of product 5b
$^1$H NMR of product 5c

$^{13}$C NMR of product 5c
$^{1}$H NMR of product 5d

$^{13}$C NMR of product 5d
$^1$H NMR of product 5e

$^{13}$C NMR of product 5e
$^1$H NMR of product 5f

$^{13}$C NMR of product 5f
$^1$H NMR of product $5g$

$^{13}$C NMR of product $5g$
$^1$H NMR of product 5h

$^{13}$C NMR of product 5h
$^{1}\text{H NMR of product 5i}$

$^{13}\text{C NMR of product 5i}$
$^1$H NMR of product 5j

$^{13}$C NMR of product 5j
$^{1}H$ NMR of product $5m$

$^{13}C$ NMR of product $5m$
$^1$H NMR of product $5n$

$^{13}$C NMR of product $5n$
$^1$H NMR of product 5o

$^{13}$C NMR of product 5o
$^1$H NMR of product 6

$^{13}$C NMR of product 6