Supporting Information

Tunable Functionalization of Saturated C-C and C-H Bonds of N,N’-Diarylpiperazines Enabled by TBN and NaNO$_2$ Systems

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General:
All solvents are anhydrous. TBN were purchased from commercial source and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. $^1$H NMR and $^{13}$C NMR (400 MHz, 600MHz and 100 MHz, 150MHz respectively) spectra were recorded in CDCl$_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. The high resolution mass spectra (HRMS) were measured on an electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry.

General Experimental Procedure
1. General experimental procedure for TBN initiated C-C bond cleavage

```
   p-Tol-\(\begin{array}{c}
   N
   \end{array}\)\(\begin{array}{c}
   N-p-Tol
   \end{array}\) \xrightarrow{TBN (1.5 equiv)} \(\begin{array}{c}
   N-p-Tol
   \end{array}\) \(\begin{array}{c}
   N-p-Tol
   \end{array}\)
```

A solution of 1a (1 mmol), 4-nitrobenzoic acid (1 mmol), NHPI (10 mol %) and H$_2$O (10 mmol) in THF (5 mL) was mixed fully, then TBN (1.5 mmol) was added dropwise under air atmosphere. The reaction solution was stirred under 45°C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1) to afford the products.

2. General experimental procedure for NaNO$_2$ initiated C-H bond activation

```
   p-Tol-\(\begin{array}{c}
   N
   \end{array}\)\(\begin{array}{c}
   N-p-Tol
   \end{array}\) \xrightarrow{NaNO$_2$ (6 equiv)} \(\begin{array}{c}
   N-p-Tol
   \end{array}\)
```

A solution of 3a (1 mmol) and 4-nitrobenzoic acid (6 mmol) in THF (5 mL) was mixed fully, then NaNO$_2$ (6 mmol) was added dropwise under air atmosphere. The reaction solution was stirred under 45°C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 10:1) to afford the products.

Optimization of reaction conditions
1. Screen of reaction conditions of TBN enabled C-C cleavage.

```
   p-Tol-\(\begin{array}{c}
   N
   \end{array}\)\(\begin{array}{c}
   N-p-Tol
   \end{array}\) \xrightarrow{TBN (x equiv)} \(\begin{array}{c}
   N-p-Tol
   \end{array}\) \(\begin{array}{c}
   N-p-Tol
   \end{array}\)
```

A solution of 1a (1 mmol) and 4-nitrobenzoic acid (1 mmol) in THF (5 mL) was mixed fully, then TBN (1.5 mmol) was added dropwise under air atmosphere. The reaction solution was stirred under 45°C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1) to afford the products.
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<th>yield (%)</th>
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<tr>
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<td>THF</td>
<td>NHPI (0.1)</td>
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<td>THF</td>
<td>NHPI (0.1)</td>
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<td>71</td>
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</table>

*a* Isolated yield in 0.5 mmol scale; *b* The yield in the parentheses was obtained in absolutely anhydrous THF; *c* Anhydrous THF used; *d* 10 equivalent water added; *e* 15 equivalent water added; *f* 20 equivalent water added.

Initially, *N,N*-diarylpiperazine 1 was chosen as the model substrate to test our hypothesis of alkyl nitrites initiated C-H and C-C activation. In the presence of 0.2 equivalent of TBN and 1 equivalent of *p*-NBA (*p*-nitrobenzoic acid) in dioxane, only trace amount of C-C cleaved product 1a was detected (entry 1). When the amount of TBN was increased to 1.2 equivalent, the desired formamide was isolated in 30% yield (entry 2). The highest yield was obtained in the presence of 1.5 equivalent of TBN (entry 3). Then, solvent screen was performed under aerobic conditions (entries 5-14), and the results showed that THF is the best solvent, giving the desired product in 48% yield (entry 14). To further increase the reaction efficiency, some additives were added (entries 15-16). When 10 mol % of TEMPO existed, the yield of the product was slightly increased to 54% (entry 15). Addition of NHPI was beneficial to this reaction, and the corresponding yield rose to 63% (entry 16). During the screen of reaction solvents, we were surprised to find that when absolutely anhydrous THF was used, the reaction efficiency was dramatically reduced (entry 14), which implied that the existence of trace amount of water is crucial to enhance the reaction efficiency. Therefore, this C-C cleavage reaction was performed in the presence of water and 10 mol % of NHPI (entries 17-19). The results showed that 10 equivalent of water gave the best reaction outcome.
and the desired formamide was isolated in 75% yield (entry 17).

2. Optimization of NaNO$_2$ initiated C-H activation.

<table>
<thead>
<tr>
<th>entry</th>
<th>oxidant (x equiv.)</th>
<th>additive (x equiv.)</th>
<th>time (h)</th>
<th>yield (%)$^a$</th>
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<td>$p$-NBA (1.0)</td>
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<td>$p$-NBA (1.5)</td>
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<td>$p$-NBA (1.0)</td>
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<td>44</td>
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<td>$p$-NBA (1.5)</td>
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<td>$p$-TsOH (1.5)</td>
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<td>2-picolinic acid (1.5)</td>
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<td>$p$-NBA (2.0)</td>
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<td>$p$-NBA (4)</td>
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<td>$p$-NBA (6)</td>
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<td>52$^d$</td>
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</table>

$^a$ Isolated yield and 0.5 mmol scale; $^b$ At 60 °C; $^c$ Air atmosphere; $^d$ Argon atmosphere.

Under TBN/O$_2$ catalyst system, only trace amount of the nitroalkene 1b was detected (entry 1). When the oxidant was changed to NaNO$_3$, no reaction occurred after stirring the reaction solution for 60 hours (entry 2). Fortunately, NaNO$_2$ displayed good reactivity, and the desired nitroalkene 1b was obtained in 44% yield (entry 3). When $p$-NBA was increased to 1.5 equivalent, the yield was increased to 58% (entry 4). Various acidic additives were then screened (entries 5-10), and $p$-NBA was still the best choice. Then different oxidant loading was examined (entries 11-16), and the highest result was obtained in the presence of 6 equivalent of NaNO$_2$ and $p$-NBA, respectively, giving the desired product 1b in 72% yield (entry 16). Comparable yield was observed when KNO$_2$ was employed as the oxidant (entry 17). The model reaction was also conducted under air and argon atmosphere, respectively, however, lower yields were obtained (entries 18-19). These results showed that dioxygen is not
the terminal oxidant but crucial to accelerate the C-H oxidation.

**Measurement of KIE**

A solution of \( d_{4}^{-}\text{1} \) (1 mmol) and 4-nitrobenzoic acid (6 mmol) in THF (5 mL) was mixed fully, then NaNO\(_{2} \) (6 mmol) was added dropwise under air atmosphere. The reaction solution was stirred under 45° C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 10:1) to afford the products. The KIE value was calculated by \(^1\)H NMR of the mixture of \( d_{3}^{-}\text{1b} \) and \( d_{2}^{-}\text{1b} \).

\( d_{4}^{-}\text{1} \): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.12 (d, \( J = 7.4 \) Hz, 4H), 6.91 (d, \( J = 7.5 \) Hz, 4H), 3.28 (s, 4H), 2.30 (s, 6H);

Mixture of \( d_{3}^{-}\text{1b} \) and \( d_{2}^{-}\text{1b} \): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.58 (s, 0.3H), 7.20 (d, \( J = 7.7 \) Hz, 2.6H), 7.10 (d, \( J = 8.1 \) Hz, 2.6H), 7.07 (d, \( J = 7.8 \) Hz, 2.6H), 6.88 (d, \( J = 7.6 \) Hz, 2.6H), 3.67 (s, 0.6H), 3.52 (s, 0.6H), 2.35 (s, 3.8H), 2.28 (s, 3.8H).
Trapping of the radical intermediate

A solution of 1 (1 mmol), 4-nitrobenzoic acid (1 mmol) and NHPI (10 mol %) in THF (5 mL) was mixed fully, then TBN (1.5 mmol) was added dropwise under air atmosphere. The reaction solution was stirred under 45°C. Then TEMPO (1 mmol) was added into the reaction solution. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1) to afford the products.

\[
\text{N} \quad \text{O} \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{1c} \\
\text{2,2,6,6-Tetramethylpiperidin-1-yl p-toly(2-(N-p-tolyformamido)ethyl)carbamate (1c)}
\]

\[\text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 8.28 (s, 1H), 7.12 (m, 8H), 3.99 (s, 2H), 3.77 (s, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 1.63 (m, 2H), 1.35 (m, 4H), 1.05 (s, 6H), 0.74 (s, 6H); \text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 162.6, 156.7, 139.2, 138.2, 136.7, 130.1, 129.6, 127.4, 125.9, 124.1, 60.2, 38.8, 31.7, 21.1, 20.9, 20.5, 16.8 (one \text{13C signal lost for overlap); HRMS (ESI): Calc’d for C}_{27}\text{H}_{38}\text{N}_3\text{O}_3\text{, 452.2908; found, 452.2889.}
Mechanism of NaNO₂ initiated C-H oxidation

\[ \text{NaNO}_2 \rightarrow \text{H}^+ + \text{NO}_2^- \]

\[ \text{NO}_2^- \rightarrow \text{NO}_2 \]

\[ \text{NO} \rightarrow \text{O}_2 \rightarrow \text{NO}_2 \]

\[ \text{[O]} \rightarrow \text{NO}_2 \]

\[ \text{[O]} \rightarrow \text{NO}_2 \]

\[ \text{[O]} \rightarrow \text{NO}_2 \]
According to reference precedents, a plausible mechanism was proposed. In the presence of acidic additive, NO$^+$ cation was liberated initially, then single electron transfer from substrate $\mathbf{1}$ to the NO$^+$ cation occurred. After deprotonation, a free radical species $\mathbf{A}$ was generated, which was further oxidized to an enamine intermediate $\mathbf{B}$. At the same time, the generated NO radical reacted with dioxygen to give a NO$_2$ radical. The electronophilic NO$_2$ radical added to the electron-rich enamine intermediate $\mathbf{B}$, providing a $\beta$-nitro radical $\mathbf{C}$. Finally, the $\beta$-nitro radical $\mathbf{C}$ underwent further oxidation, giving the nitroalkene product $\mathbf{1b}$.

**NOESY of the product 27b**

When unsymmetric substrates were employed, the NaNO$_2$ initiated C-H oxidation occurred selectively. In the reaction of substrate $\mathbf{27}$, only one product $\mathbf{27b}$ was isolated. According to NOESY experiment, the structure of $\mathbf{27b}$ was fully identified.

**References**


**Analytical data for compounds**
N,N’-(Ethane-1,2-diy)bis(N-p-tolylformamide) (1a)
Compound 1a was isolated in 78% yield (231 mg, white crystal); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25 (s, 2H), 7.15 (d, \(J = 8.0\) Hz, 4H), 6.94 (d, \(J = 8.4\) Hz, 4H), 3.97 (s, 4H), 2.34 (s, 6H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.6, 138.1, 136.8, 130.2, 123.7, 43.2, 20.9; HRMS (ESI): Calc’d for C\(_{18}\)H\(_{20}\)N\(_2\)O\(_2^+\), 319.1417; found, 319.1430.

N-(4-Fluorophenyl)-N-(2-(N-p-tolylformamido)ethyl)formamide (2a)
Compound 2a was isolated in 70% yield (210 mg, white crystal); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.22 (s, 1H), 8.20 (s, 1H), 7.14 (d, \(J = 8.0\) Hz, 2H), 7.03 (d, \(J = 6.4\) Hz, 4H), 6.92 (d, \(J = 8.4\) Hz, 2H), 3.94 (s, 4H), 2.32 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.6, 162.4, 161.3 (d, \(J = 247.1\) Hz), 137.0, 136.9, 136.8 (d, \(J = 3.0\) Hz), 130.2, 125.9 (d, \(J = 8.5\) Hz), 123.7, 116.5 (d, \(J = 22.7\) Hz), 43.5, 43.2, 20.9; HRMS (ESI): Calc’d for C\(_{17}\)H\(_{18}\)FN\(_2\)O\(_2^+\), 301.1347; found, 301.1357.

N-(4-Chlorophenyl)-N-(2-(N-p-tolylformamido)ethyl)formamide (3a)
Compound 3a was isolated in 69% yield (218 mg, white crystal); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.24 (s, 1H), 8.22 (s, 1H), 7.30 (d, \(J = 8.7\) Hz, 2H), 7.13 (d, \(J = 8.1\) Hz, 2H), 6.99 (d, \(J = 8.7\) Hz, 2H), 6.91 (d, \(J = 8.3\) Hz, 2H), 3.95 (s, 4H), 2.32 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.6, 162.2, 139.3, 138.0, 136.9, 132.5, 130.2, 129.7, 124.8, 123.6, 43.2, 20.9; HRMS (ESI): Calc’d for C\(_{17}\)H\(_{18}\)ClN\(_2\)O\(_2^+\), 317.1051; found, 317.1043.

N-(4-Bromophenyl)-N-(2-(N-p-tolylformamido)ethyl)formamide (4a)
Compound 4a was isolated in 75% yield (270 mg, light yellow crystal); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.27 (s, 1H), 8.24 (s, 1H), 7.47 (d, \(J = 8.8\) Hz, 2H), 7.15 (d, \(J = 8.0\) Hz, 2H), 6.93 (t, \(J = 9.1\) Hz, 4H),
3.97 (s, 4H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 162.1, 139.8, 138.0, 136.9, 132.7, 130.2, 125.0, 123.6, 120.3, 43.3, 43.2, 20.9; HRMS (ESI): Calc’d for C$_{17}$H$_{17}$BrN$_2$NaO$_2^+$, 383.0366; found, 383.0373.

$N$-$(4$-Iodophenyl$)$-$N$-$(2$-$(N$-p$-tolylformamido)ethyl$)$formamide (5a)

Compound 5a was isolated in 71% yield (290 mg, light yellow crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (s, 1H), 8.23 (s, 1H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 3.96 (s, 4H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 162.1, 140.4, 138.7, 138.0, 136.9, 130.2, 125.2, 91.2, 43.3, 43.2, 20.9; HRMS (ESI): Calc’d for C$_{17}$H$_{17}$IN$_2$NaO$_2^+$, 431.0227; found, 431.0223.

$N$-$(4$-Methoxyphenyl$)$-$N$-$(2$-$(N$-p$-tolylformamido)ethyl$)$formamide (6a)

Compound 6a was isolated in 15% yield (47 mg, white crystal); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.25 (s, 1H), 8.19 (s, 1H), 7.16 (d, $J = 7.7$ Hz, 2H), $\delta$ 6.99 (d, $J = 7.8$ Hz, 2H), 6.96 (d, $J = 7.4$ Hz, 2H), 6.87 (d, $J = 7.9$ Hz, 2H), 3.95 (dd, $J = 13.0$, 5.1 Hz, 4H), 3.81 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 162.8, 162.7, 158.6, 138.1, 136.9, 133.6, 130.2, 125.9, 123.9, 114.8, 55.6, 43.6, 43.3, 20.9; HRMS (ESI): Calc’d for C$_{18}$H$_{20}$N$_2$O$_3^+$, 335.1366; found, 335.1372.

$N$-$(4$-Acetylphenyl$)$-$N$-$(2$-$(N$-p$-tolylformamido)ethyl$)$formamide (7a)

Compound 7a was isolated in 34% yield (110 mg, light yellow crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 (s, 1H), 8.23 (s, 1H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.17 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 8.3$ Hz, 2H), 4.08 – 3.96 (m, 4H), 2.57 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.7, 162.7, 162.1, 144.7, 138.0, 137.0, 134.8, 130.3, 130.0, 123.5, 121.9, 43.3, 42.7, 26.6, 20.9; HRMS (ESI): Calc’d for C$_{19}$H$_{20}$N$_2$NaO$_2^+$, 347.1366; found, 347.1376.
Methyl 4-((N-(2-(N-p-tolylformamido)ethyl)formamido)benzoate (8a)

Compound 8a was isolated in 47% yield (160 mg, light yellow crystal); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.40\) (s, 1H), 8.23 (s, 1H), 8.01 (d, \(J = 8.8\) Hz, 2H), 7.14 – 7.10 (m, 4H), 6.88 (d, \(J = 8.4\) Hz, 2H), 4.06 – 3.97 (m, 4H), 3.89 (s, 3H), 2.32 (s, 3H); \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 166.1, 162.6, 162.1, 144.6, 138.0, 136.9, 131.2, 130.2, 128.0, 123.4, 121.9, 52.3, 43.3, 42.8, 20.9\; HRMS (ESI): Calc’d for C\(_{19}\)H\(_{20}\)N\(_2\)NaO\(_4\)^+, 363.1315; found , 363.1324.

N-(4-(tert-Butyl)phenyl)-N-(2-(N-p-tolylformamido)ethyl)formamide (9a)

Compound 9a was isolated in 60% yield (203 mg, white crystal); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.27\) (s, 1H), 8.23 (s, 1H), 7.36 (d, \(J = 8.7\) Hz, 2H), 7.12 (dd, \(J = 8.5, 0.5\) Hz, 2H), 6.99 (d, \(J = 8.7\) Hz, 2H), 6.89 (d, \(J = 8.4\) Hz, 2H), 3.98 (m, 4H), 2.32 (s, 3H), 1.31 (s, 9H); \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 162.7, 162.6, 150.0, 138.1, 138.0, 136.8, 130.1, 126.5, 123.6, 123.3, 43.3, 43.2, 34.5, 31.3, 20.9; HRMS (ESI): Calc’d for C\(_{21}\)H\(_{26}\)N\(_2\)NaO\(_2\)^+, 361.1886; found , 361.1899.

N-(4-Formylphenyl)-N-(2-(N-p-tolylformamido)ethyl)formamide (10a)

Compound 10a was isolated in 49% yield (1521 mg, yellow crystal); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 10.00\) (s, 1H), 8.52 (s, 1H), 8.28 (s, 1H), 7.92 (s, 2H), 7.29 (s, 2H), 7.18 (s, 2H), 6.94 (s, 2H), 4.11 (s, 2H), 4.04 (s, 2H), 2.36 (s, 3H); \(^1^3\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 190.8, 162.7, 162.0, 145.9, 138.0, 137.0, 134.1, 131.3, 130.3, 123.5, 122.2, 43.3, 42.8, 20.9; HRMS (ESI): Calc’d for C\(_{18}\)H\(_{18}\)N\(_2\)NaO\(_3\)^+, 333.1210; found , 333.1209.
**N-(3-Chlorophenyl)-N-(2-(N-p-tolyiformamido)ethyl)formamide (11a)**

Compound 11a was isolated in 50% yield (158 mg, white crystal); 1H NMR (400 MHz, CDCl₃) δ 8.21 (s, 2H), 7.35 (dd, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.01 – 6.98 (m, 1H), 6.96 (t, J = 2.0 Hz, 1H), 6.86 (d, J = 8.4 Hz, 2H), 3.96 (m, 4H), 2.32 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 162.6, 162.2, 141.9, 130.9, 130.3, 129.7, 126.5, 123.5, 123.0, 121.9, 43.1, 20.9; HRMS (ESI): Calc’d for C₁₇H₁₇ClN₂O₂⁺, 339.0871; found, 339.0877.

**N-(3-Bromophenyl)-N-(2-(N-p-tolyiformamido)ethyl)formamide (12a)**

Compound 12a was isolated in 53% yield (191 mg, white crystal); 1H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 8.23 (s, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.22 (dd, J = 8.1, 1.9 Hz, 1H), 7.16 – 7.13 (m, 2H), 6.97 (dd, J = 7.9, 2.2 Hz, 1H), 6.91 – 6.85 (m, 3H), 3.98 (m, 4H), 2.34 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 162.6, 162.2, 141.8, 138.0, 136.9, 135.2, 130.6, 130.3, 126.8, 123.6, 121.4, 43.3, 43.1, 20.9; HRMS (ESI): Calc’d for C₁₇H₁₇BrN₂O₂⁺, 383.0366; found, 383.0369.

**N-(3,4-Dimethylphenyl)-N-(2-(N-p-tolyiformamido)ethyl)formamide (13a)**

Compound 13a was isolated in 55% yield (171 mg, white crystal); 1H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 8.20 (s, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.1 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.77 (dd, J = 8.0, 2.4 Hz, 1H), 6.68 (d, J = 2.1 Hz, 1H), 3.96 (m, 4H), 2.34 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 162.6, 162.2, 138.2, 138.0, 136.7, 135.4, 130.5, 130.1, 125.1, 123.7, 121.2, 43.3, 43.2, 20.9, 19.8, 19.2 (one 13C signal lost for overlap); HRMS (ESI): Calc’d for C₁₉H₂₂N₂O₂⁺, 333.1573; found, 333.1582.
**N-(3,5-Dimethylphenyl)-N-(2-(N-p-tolyformamido)ethyl)formamide (14a)**

Compound 14a was isolated in 71% yield (220 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 (s, 1H), 8.22 (s, 1H), 7.15 (d, $J$ = 8.0 Hz, 2H), 6.94 – 6.87 (m, 3H), 6.54 (s, 2H), 3.97 (m, 4H), 2.35 (s, 3H), 2.27 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.7, 162.6, 140.4, 139.3, 138.2, 136.7, 130.1, 128.5, 123.7, 121.5, 43.3, 43.2, 21.2, 20.9; HRMS (ESI): Calc’d for C$_{19}$H$_{22}$N$_2$NaO$_2^+$, 333.1573; found, 333.1575.

**N-(3-Chloro-4-methoxyphenyl)-N-(2-(N-p-tolyformamido)ethyl)formamide (15a)**

Compound 15a was isolated in 51% yield (176 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (s, 1H), 8.12 (s, 1H), 7.15 (d, $J$ = 8.0 Hz, 2H), 6.94 (d, $J$ = 2.6 Hz, 1H), 6.92 (d, $J$ = 8.3 Hz, 2H), 6.89 (s, 1H), 6.86 (d, $J$ = 2.8 Hz, 1H), 3.92 (s, 4H), 3.87 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 162.5, 154.1, 138.0, 137.0, 133.7, 130.2, 126.4, 123.8, 123.8, 123.0, 112.4, 56.4, 43.6, 43.1, 20.9; HRMS (ESI): Calc’d for C$_{18}$H$_{19}$N$_2$NaO$_3^+$, 369.0976; found, 369.0982.

**N-(2-Fluoro-4-methylphenyl)-N-(2-(N-p-tolyformamido)ethyl)formamide (16a)**

Compound 16a was isolated in 45% yield (141 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (s, 1H), 8.09 (d, $J$ = 1.7 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 2H), 6.99 – 6.92 (m, 5H), 3.98 – 3.84 (m, 4H), 2.34 (d, $J$ = 4.2 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.1 (d, $J$ = 1.8 Hz), 162.6, 157.3 (d, $J$ = 249.5 Hz), 140.3 (d, $J$ = 7.6 Hz), 137.9, 136.9, 130.2, 128.3 (two $^{13}$C), 125.5 (d, $J$ = 3.4 Hz), 123.9, 117.3 (d, $J$ = 19.9 Hz), 43.2 (d, $J$ = 2.5 Hz), 43.0, 21.1 (d, $J$ = 1.4 Hz), 20.9; HRMS (ESI): Calc’d for C$_{18}$H$_{19}$FN$_2$NaO$_2^+$, 337.1323; found, 337.1328.

**N-(3-Bromo-4-methylphenyl)-N-(2-(N-p-tolyformamido)ethyl)formamide (17a)**

Compound 17a was isolated in 55% yield (206 mg, yellow crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (s, 1H), 8.17 (s, 1H), 7.19 (d, $J$ = 8.2 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 2H), 6.98 (d, $J$ = 2.3 Hz, 1H), 6.93 – 6.88 (m, 3H), 3.94 (m, 4H), 2.34 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 162.3, 139.2, 138.0, 136.9, 136.6, 131.4, 130.2, 127.4, 125.2, 123.6, 122.4, 43.3, 43.2, 22.3, 20.9; HRMS (ESI): Calc’d for C$_{18}$H$_{19}$N$_2$BrNaO$_2^+$, 397.0522; found, 397.0526.
**N-(3-Chloro-4-methylphenyl)-N-(2-(N-p-tolylformamido)ethyl)formamide (18a)**

Compound 18a was isolated in 58% yield (191 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (s, 1H), 8.19 (s, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 7.14 (dd, $J = 8.5$, 0.6 Hz, 2H), 6.92 – 6.89 (m, 2H), 6.87 (dd, $J = 8.0$, 2.3 Hz, 1H), 6.84 (d, $J = 2.3$ Hz, 1H), 3.95 (m, 4H), 2.33 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 162.3, 139.3, 138.0, 136.9, 135.0, 134.8, 131.6, 130.2, 124.2, 123.6, 121.8, 43.3, 43.2, 20.9, 19.5; HRMS (ESI): Calc’d for C$_{18}$H$_{19}$N$_2$ClNaO$_2^+$, 353.1027; found, 353.1036.

**N-(Naphthalen-2-yl)-N-(2-(N-p-tolylformamido)ethyl)formamide (19a)**

Compound 19a was isolated in 41% yield (136 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38 (s, 1H), 8.24 (s, 1H), 7.87 – 7.79 (m, 2H), 7.73 – 7.67 (m, 1H), 7.52 – 7.47 (m, 2H), 7.27 (d, $J = 2.2$ Hz, 1H), 7.22 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.10 (dd, $J = 8.5$, 0.6 Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 4.12 (t, $J = 6.5$ Hz, 2H), 4.12 (t, $J = 6.0$ Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.8, 162.7, 138.2, 137.9, 136.8, 133.5, 131.8, 130.2, 129.8, 127.7 (two $^{13}$C), 127.0, 126.3, 123.7, 121.9, 121.7, 43.4, 43.3, 20.9; HRMS (ESI): Calc’d for C$_{21}$H$_{20}$N$_2$NaO$_2^+$, 355.1417; found, 355.1428.

**N,N’-(Ethane-1,2-diyl)bis(N-(4-chlorophenyl)formamide) (21a)**

Compound 21a was isolated in 81% yield (272 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (s, 2H), 7.07 (d, $J = 6.3$ Hz, 8H), 3.95 (s, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3, 139.1, 132.7, 129.9, 124.7, 43.2; HRMS (ESI): Calc’d for C$_{16}$H$_{14}$Cl$_2$N$_2$NaO$_2^+$, 359.0325; found, 359.0318.

**N,N’-(Ethane-1,2-diyl)bis(N-(4-fluorophenyl)formamide) (22a)**
Compound 22a was isolated in 69% yield (210 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (s, 2H), 7.34 (d, $J = 8.2$ Hz, 4H), 7.01 (d, $J = 8.2$ Hz, 4H), 3.97 (s, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.5, 161.4 (d, $J = 247.5$ Hz), 136.6 (d, $J = 3.0$ Hz), 126.0 (d, $J = 8.5$ Hz), 116.6 (d, $J = 22.8$ Hz), 43.5; HRMS (ESI): Calc’d for C$_{16}$H$_{14}$F$_2$N$_2$NaO$_2^2$+, 327.0916; found, 327.0922.

\[
\begin{array}{c}
\text{N,N'-\text{(Ethane-1,2-diyl)bis(N-m-toly1formamide) (23a)}}
\end{array}
\]

Compound 23a was isolated in 46% yield (136 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (s, 2H), 7.22 (t, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 7.5$ Hz, 2H), 6.82 (d, $J = 7.7$ Hz, 2H), 6.75 (s, 2H), 4.00 (s, 4H), 2.31 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 140.6, 139.6, 129.4, 127.5, 124.2, 120.6, 43.2, 21.4; HRMS (ESI): Calc’d for C$_{18}$H$_{20}$N$_2$NaO$_2^2$+, 319.1417; found, 319.1420.

\[
\begin{array}{c}
\text{N,N'-\text{(Ethane-1,2-diyl)bis(N-(3,4-dimethylphenyl)formamide) (24a)}}
\end{array}
\]

Compound 24a was isolated in 42% yield (136 mg, white crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (s, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.79 (d, $J = 8.1$ Hz, 2H), 6.72 (s, 2H), 3.96 (s, 4H), 2.25 (s, 6H), 2.22 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 138.4, 138.0, 135.4, 130.5, 125.1, 121.2, 43.3, 19.9, 19.2; HRMS (ESI): Calc’d for C$_{20}$H$_{24}$N$_2$NaO$_2^2$+, 347.1730; found, 347.1739.

\[
\begin{array}{c}
\text{Ethyl 2-methyl-3-\text{(4-(N-(2-(N-p-toly1formamido)ethyl)formamido)phenyl)acrylate (25a)}}
\end{array}
\]

Compound 25a was isolated in 75% yield (296 mg, yellow crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37 (s, 1H), 8.26 (s, 1H), 7.63 (s, 1H), 7.40 (d, $J = 7.6$ Hz, 2H), 7.15 (d, $J = 7.5$ Hz, 2H), 7.10 (d, $J = 7.5$ Hz, 2H), 6.92 (d, $J = 7.3$ Hz, 2H), 4.27 (q, $J = 6.9$ Hz, 2H), 4.02 (s, 4H), 2.34 (s, 3H), 2.11 (s, 3H), 1.34 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.4, 162.7, 162.3, 140.4, 138.0, 137.2, 136.9, 134.3, 131.0, 130.2, 129.2, 123.5, 122.8, 61.0, 43.3, 43.0, 20.9, 14.3, 14.1; HRMS (ESI): Calc’d for C$_{23}$H$_{26}$N$_2$NaO$_4^2$+, 417.1785; found, 417.1792.

\[
\begin{array}{c}
\text{N,N'-\text{(Ethane-1,2-diyl)bis(N-m-toly1formamide) (23a)}}
\end{array}
\]

\[
\begin{array}{c}
\text{N,N'-\text{(Ethane-1,2-diyl)bis(N-(3,4-dimethylphenyl)formamide) (24a)}}
\end{array}
\]

\[
\begin{array}{c}
\text{Ethyl 2-methyl-3-\text{(4-(N-(2-(N-p-toly1formamido)ethyl)formamido)phenyl)acrylate (25a)}}
\end{array}
\]
**N-(2-(Nitroso(p-toly)amino)ethyl)-N-(p-toly)formamide (26a)**

Compound 26a was isolated in 99% yield (294 mg, colorless oil); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (s, 1H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 6.93 (d, $J = 8.4$ Hz, 2H), 4.32 – 4.19 (m, 2H), 3.98 – 3.79 (m, 2H), 2.37 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 139.0, 137.9, 137.4, 136.9, 130.3, 130.1, 123.2, 119.3, 42.0 (two $^{13}$C), 20.9 (two $^{13}$C); HRMS (ESI): Calc’d for C$_{17}$H$_{19}$N$_3$NaO$_2^+$, 320.1370; found, 320.1369.

![Chemical Structure of 26a](image)

**5-Nitro-1,4-di-p-tolyl-1,2,3,4-tetrahydropyrazine (1b)**

Compound 1b was isolated in 72% yield (222 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (s, 1H), 7.20 (d, $J = 7.6$ Hz, 2H), 7.11 (d, $J = 7.6$ Hz, 2H), 7.07 (d, $J = 7.6$ Hz, 2H), 6.89 (d, $J = 7.6$ Hz, 2H), 3.69 (s, 2H), 3.54 (s, 2H), 2.35 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.8, 141.5, 135.1, 132.8, 130.4, 130.3, 130.2, 123.0, 120.4, 118.7, 48.9, 44.3, 20.8, 20.7; HRMS (ESI): Calc’d for C$_{18}$H$_{19}$N$_3$NaO$_2^+$, 332.1369; found, 332.1365.

![Chemical Structure of 1b](image)

**5-Nitro-1,4-di-m-tolyl-1,2,3,4-tetrahydropyrazine (23b)**

Compound 23b was isolated in 50% yield (155 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (s, 1H), 7.28 (t, $J = 7.8$ Hz, 1H), 7.18 (t, $J = 7.0$ Hz, 1H), 7.04 – 6.94 (m, 3H), 6.85 (d, $J = 7.4$ Hz, 1H), 6.78 (s, 2H), 3.71 (s, 2H), 3.56 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.1, 143.7, 140.0, 139.3, 130.0, 129.6, 129.2, 126.0, 124.1, 121.0, 119.4, 117.5, 115.8, 48.7, 44.0, 21.6, 21.6 (one $^{13}$C signal lost for overlap); HRMS (ESI): Calc’d for C$_{18}$H$_{19}$N$_3$NaO$_2^+$, 332.1369; found, 332.1365.

![Chemical Structure of 23b](image)

**1,4-Bis(4-fluorophenyl)-5-nitro-1,2,3,4-tetrahydropyrazine (22b)**
Compound 22b was isolated in 49% yield (155 mg, red crystal); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.48 (s, 1H), 7.21 – 7.04 (m, 4H), 7.06 – 6.87 (m, 4H), 3.66 (s, 2H), 3.53 (s, 2H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.4, 160.1 (d, \(J = 246.2\) Hz), 159.1 (d, \(J = 242.9\) Hz), 143.4 (d, \(J = 2.4\) Hz), 140.1 (d, \(J = 2.8\) Hz), 130.2, 122.1 (d, \(J = 8.1\) Hz), 120.7 (d, \(J = 8.3\) Hz), 116.7 (d, \(J = 23.0\) Hz), 116.1 (d, \(J = 22.7\) Hz), 49.2, 44.5; HRMS (ESI): Calc’d for C\(_{16}\)H\(_{13}\)F\(_2\)N\(_3\)NaO\(_2^+\), 340.0868; found, 340.0862.

\[
\text{1,4-Bis(3,4-dimethylphenyl)-5-nitro-1,2,3,4-tetrahydropyrazine (24b)}
\]

Compound 24b was isolated in 49% yield (165 mg, yellow crystal); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.59 (s, 1H), 7.15 (d, \(J = 8.2\) Hz, 1H), 7.05 (d, \(J = 7.9\) Hz, 1H), 6.98 (s, 1H), 6.91 (d, \(J = 8.1\) Hz, 1H), 6.78 (s, 1H), 6.73 (d, \(J = 8.1\) Hz, 1H), 3.68 (s, 2H), 3.54 (s, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.2, 141.7, 138.3, 137.7, 133.9, 131.6, 130.7, 130.5, 130.5, 130.1, 121.8, 120.1, 117.8, 116.2, 48.9, 44.3, 20.1, 19.2, 19.0. HRMS (ESI): Calc’d for C\(_{20}\)H\(_{23}\)N\(_3\)NaO\(_2^+\), 360.1682; found, 360.1681.

\[
\text{4-(4-Fluorophenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (2b)}
\]

Compound 2b was isolated in 58% yield (182 mg, red oil); Mixture of two isomers (ratio: 3 : 1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.58 (s, 1H), 8.49 (s, 0.3H), 7.29 – 7.17 (m, 2.6H), 7.09 (m, 3.4H), 7.04 – 6.91 (m, 3.8H), 6.88 (d, \(J = 7.7\) Hz, 0.6H), 3.67 (s, 2.6H), 3.55 (s, 2.6H), 2.35 (s, 3H), 2.29 (s, 1H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.2, 157.8, 144.7, 143.4, 141.4, 135.3, 130.5, 130.4, 130.0, 129.8, 122.0 (two \(^1\)C), 120.5 (two \(^1\)C), 118.8, 116.8, 116.5, 116.2, 116.0, 49.2, 49.0, 44.5, 44.2, 20.8, 20.7; HRMS (ESI): Calc’d for C\(_{16}\)H\(_{16}\)FN\(_3\)NaO\(_2^+\), 336.1119; found, 336.1125.

\[
\text{4-(4-Chlorophenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (3b)}
\]

Compound 3b was isolated in 81% yield (266 mg, red crystal); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.58 (d, \(J = 0.8\) Hz, 1H), 7.24 (d, \(J = 7.6\) Hz, 2H), 7.21 (d, \(J = 7.9\) Hz, 2H), 7.07 (d, \(J = 7.4\) Hz, 2H), 6.89 (d, \(J = 7.2\) Hz, 2H), 3.70 (s, 2H), 3.55 (s, 2H), 2.35 (s, 3H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.6, 141.3, 135.5,
131.0, 130.4, 129.4, 128.2, 121.5, 118.8, 48.5, 44.6, 20.8 (one $^{13}$C signal lost for overlap); HRMS (ESI): Calc'd for C$_{17}$H$_{16}$ClN$_3$NaO$_2^+$, 352.0823; found, 352.0822.

4-(4-Bromophenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (4b)

Compound 4b was isolated in 68% yield (254 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.58 (d, $J = 0.9$ Hz, 1H), 7.38 (d, $J = 7.2$ Hz, 2H), 7.21 (d, $J = 7.4$ Hz, 2H), 7.07 (d, $J = 7.1$ Hz, 2H), 6.83 (d, $J = 7.2$ Hz, 2H), 3.70 (s, 2H), 3.55 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.1, 141.3, 135.5, 132.3, 131.0, 130.4, 129.2, 121.8, 118.9, 115.8, 48.4, 44.7, 20.8; HRMS (ESI): Calc'd for C$_{17}$H$_{16}$BrN$_3$NaO$_2^+$, 396.0318; found, 396.0316.

4-(4-Iodophenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (5b)

Compound 5b was isolated in 68% yield (286 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 (s, 1H), 7.57 (d, $J = 7.3$ Hz, 2H), 7.21 (d, $J = 7.7$ Hz, 2H), 7.07 (d, $J = 7.3$ Hz, 2H), 6.71 (d, $J = 7.4$ Hz, 2H), 3.70 (d, $J = 3.2$ Hz, 2H), 3.56 (d, $J = 3.4$ Hz, 2H), 2.35 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.7, 141.3, 138.2, 135.5, 131.1, 130.4, 129.1, 122.2, 118.9, 86.2, 48.2, 44.8, 20.8; HRMS (ESI): Calc'd for C$_{17}$H$_{16}$IN$_3$NaO$_2^+$, 444.0179; found, 444.0182.

4-(4-Methoxyphenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (6b)

Compound 6b was isolated in 65% yield (211 mg, yellow crystal); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (s, 0.4H), 8.51 (s, 1H), 7.18 (t, $J = 8.5$ Hz, 1.2H), 7.08 (dd, $J = 14.0$, 7.5 Hz, 5H), 6.99 – 6.89 (m, 3H), 6.89 – 6.75 (m, 3H), 3.79 (s, 3H), 3.72 (s, 1.3H), 3.66 (s, 2H), 3.61 (s, 1H), 3.50 (d, $J = 2.0$ Hz, 3H), 2.34 (s, 1H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.4, 155.9, 144.8, 141.5, 140.9, 137.4, 135.1, 132.6, 131.2, 130.3, 130.2, 130.0, 129.8, 125.3, 122.0, 120.7, 120.3, 118.7, 114.9, 114.7, 55.6, 55.5, 49.4, 48.7, 44.8, 43.9, 20.8, 20.7; HRMS (ESI): Calc’d for C$_{18}$H$_{19}$N$_3$NaO$_3^+$, 348.1319; found, 348.1324.
1-(4-(6-Nitro-4-(p-tolyl)-3,4-dihydropyrazin-1(2H)-yl)phenyl)ethan-1-one (7b)

Compound 7b was isolated in 29% yield (98 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59 (s, 1H), 7.89 (d, $J = 7.8$ Hz, 2H), 7.20 (d, $J = 7.3$ Hz, 2H), 7.07 (d, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 7.7$ Hz, 2H), 3.84 (s, 2H), 3.61 (s, 2H), 2.52 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.8, 150.3, 141.1, 135.8, 131.8, 131.3, 130.4, 130.0, 128.5, 119.0, 118.7, 47.0, 45.8, 26.4, 20.8; HRMS (ESI): Calc’d for C$_{19}$H$_{19}$N$_3$NaO$_3^+$, 360.1319; found, 360.1315.

Methyl 4-(6-nitro-4-(p-tolyl)-3,4-dihydropyrazin-1(2H)-yl)benzoate (8b)

Compound 8b was isolated in 20% yield (71 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59 (s, 1H), 7.95 (d, $J = 7.5$ Hz, 2H), 7.20 (d, $J = 7.6$ Hz, 2H), 7.07 (d, $J = 7.4$ Hz, 2H), 6.92 (d, $J = 7.6$ Hz, 2H), 3.86 (s, 3H), 3.82 (s, 2H), 3.60 (s, 2H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.7, 150.3, 141.2, 135.7, 131.6, 131.1, 130.4, 128.7, 123.9, 118.9, 118.7, 51.9, 47.2, 45.6, 20.8; HRMS (ESI): Calc’d for C$_{19}$H$_{19}$N$_3$NaO$_4^+$, 376.1268; found, 376.1261.

4-(6-Nitro-4-(p-tolyl)-3,4-dihydropyrazin-1(2H)-yl)benzaldehyde (10b)

Compound 10b was isolated in 38% yield (123 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.83 (s, 1H), 8.59 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 7.5$ Hz, 2H), 7.08 (d, $J = 7.7$ Hz, 2H), 6.97 (d, $J = 8.3$ Hz, 2H), 3.86 (s, 2H), 3.63 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.8, 151.3, 141.0, 136.0, 132.1, 131.4, 130.6, 130.5, 128.2, 119.0, 118.9, 46.7, 46.1, 20.8; HRMS (ESI): Calc’d for C$_{18}$H$_{17}$N$_3$NaO$_3^+$, 346.1162; found, 346.1157.
4-(6-Nitro-4-(p-tolyl)-3,4-dihydropyrazin-1(2H)-yl)benzonitrile (27b)

Compound 27b was isolated in 36% yield (115 mg, red crystal); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.59 (s, 1H), 7.54 (d, \( J = 7.4 \) Hz, 2H), 7.21 (d, \( J = 7.6 \) Hz, 2H), 7.08 (d, \( J = 7.3 \) Hz, 2H), 6.93 (d, \( J = 7.4 \) Hz, 2H), 3.83 (s, 2H), 3.63 (s, 2H), 2.34 (s, 3H); \( ^1^C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 149.8, 141.0, 136.2, 133.4, 132.3, 130.5, 127.8, 119.3, 119.1 (two \( ^1^C \)), 104.9, 46.8, 46.0, 20.8; HRMS (ESI): Calc’d for C\(_{18}\)H\(_{16}\)N\(_4\)NaO\(_2^+\), 343.1165; found, 343.1169.

4-(4-(tert-Butyl)phenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (9b)

Compound 9b was isolated in 65% yield (228 mg, red oil); Mixture of two isomers (ratio: 1 : 1); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.61 (s, 1H), 8.59 (s, 1H), 7.43 (d, \( J = 7.3 \) Hz, 2H), 7.30 (d, \( J = 7.3 \) Hz, 2H), 7.20 (d, \( J = 7.5 \) Hz, 2H), 7.16 – 7.04 (m, 6H), 6.89 (t, \( J = 8.5 \) Hz, 4H), 3.69 (s, 4H), 3.54 (s, 4H), 2.34 (s, 3H), 2.28 (s, 3H), 1.33 (s, 9H), 1.29 (s, 9H); \( ^1^C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.4, 145.8, 144.8, 144.6, 141.4, 141.2, 135.1, 132.7, 130.5, 130.3 (two \( ^1^C \)), 130.3, 130.0, 126.7, 126.3, 120.4, 119.9, 118.7, 118.4, 48.9, 48.7, 44.4, 44.2, 34.5, 34.2, 31.4, 31.3, 20.8, 20.7 (one \( ^1^C \) signal lost for overlap); HRMS (ESI): Calc’d for C\(_{21}\)H\(_{25}\)N\(_3\)NaO\(_2^+\), 374.1839; found, 374.1843.

4-(3-Chlorophenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (11b)

Compound 11b was isolated in 47% yield (155 mg, red crystal); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.59 (s, 1H), 7.22 – 7.19 (m, 3H), 7.07 (d, \( J = 7.6 \) Hz, 2H), 6.99 (d, \( J = 7.8 \) Hz, 1H), 6.94 (s, 1H), 6.84 (d, \( J = 8.2 \) Hz, 1H), 3.73 (s, 2H), 3.57 (s, 2H), 2.35 (s, 3H); \( ^1^C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.2, 141.3, 135.8, 135.1, 131.2, 130.4, 129.0, 123.1, 120.3, 118.9, 118.3, 48.3, 44.9, 20.8; HRMS (ESI): Calc’d for C\(_{17}\)H\(_{16}\)ClN\(_3\)NaO\(_2^+\), 352.0823; found, 352.0817.

4-(3-Bromophenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (12b)

Compound 12b was isolated in 49% yield (183 mg, red crystal); \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.58 (s, 1H), 7.21 (d, \( J = 7.6 \) Hz, 2H), 7.14 – 7.05 (m, 5H), 6.87 (d, \( J = 6.8 \) Hz, 1H), 3.71 (s, 2H), 3.56 (s, 2H), 2.34 (s, 3H); \( ^1^C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.3, 141.2, 135.6, 131.3, 130.6, 130.4, 128.9, 126.0, 123.1, 118.9, 118.8, 48.2, 44.9, 20.8 (one \( ^1^C \) signal lost for overlap); HRMS (ESI): Calc’d for C\(_{17}\)H\(_{16}\)BrN\(_3\)NaO\(_2^+\), 396.0318; found, 396.0320.
4-(3,4-Dimethylphenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (13b)

Compound 13b was isolated in 62% yield (200 mg, yellow oil); Mixture of two isomers (ratio: 1.5 : 1); 
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.59 (s, 1H), 8.58 (s, 0.66H), 7.20 (d, \(J = 7.7\) Hz, 1.6H), 7.15 (d, \(J = 8.2\) Hz, 1.2H), 7.07 (m, 4.1H), 6.98 (s, 1.2H), 6.89 (m, 3.2H), 6.78 (s, 1H), 6.72 (d, \(J = 8.1\) Hz, 1H), 3.67 (s, 3.6H), 3.53 (s, 3.6H), 2.35 (s, 2.3H), 2.28 (s, 6H), 2.25 (s, 3H), 2.21 (s, 2H), 2.19 (s, 2.2H); 
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.2, 144.9, 141.7, 141.5, 138.3, 137.7, 135.1, 134.0, 132.7, 131.5, 130.7 (two \(^{13}\)C), 130.5, 130.3 (two \(^{13}\)C), 130.1, 130.0 (two \(^{13}\)C), 121.8, 120.3, 120.1, 118.7, 117.8, 116.2, 48.9 (two \(^{13}\)C), 44.3, 44.2, 20.8, 20.7, 20.1, 20.1, 19.2, 19.0; HRMS (ESI): Calc’d for C\(_{19}\)H\(_{21}\)N\(_3\)NaO\(_2^+\), 3346.1526; found, 346.1520.

4-(2,4-Dimethylphenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (20b)

Compound 20b was isolated in 60% yield (194 mg, yellow oil); Mixture of two isomers (ratio: 2.0 : 1); 
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.59 (s, 1H), 8.58 (s, 0.5H), 7.20 (d, \(J = 7.6\) Hz, 1.5H), 7.15 (d, \(J = 8.3\) Hz, 1.5H), 7.08 (m, 3.7H), 6.98 (s, 1.5H), 6.89 (m, 3H), 6.78 (s, 0.8H), 6.73 (d, \(J = 8.2\) Hz, 0.8H), 3.68 (s, 3H), 3.53 (s, 3H), 2.35 (s, 2H), 2.29 (s, 6H), 2.25 (s, 3H), 2.21 (s, 2H), 2.19 (s, 2H); 
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.2, 144.9, 141.7, 141.5, 138.3, 137.7, 135.1, 133.9, 132.7, 131.6, 130.7 (two \(^{13}\)C), 130.5, 130.3, 130.0, 129.2, 121.8, 120.3, 120.1, 119.4, 118.7, 117.8, 116.2, 115.1, 48.9 (two \(^{13}\)C), 44.3, 44.2, 20.8, 20.7, 20.1 (two \(^{13}\)C), 19.2, 19.0; HRMS (ESI): Calc’d for C\(_{19}\)H\(_{21}\)N\(_3\)NaO\(_2^+\), 346.1526; found, 346.1522.

4-(2-Isopropylphenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (28b)

Compound 28b was isolated in 49% yield (165 mg, yellow oil); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (s, 1H), 7.37 (m, 2H), 7.24 (t, \(J = 6.7\) Hz, 1H), 7.12 (m, 3H), 6.92 (d, \(J = 7.5\) Hz, 2H), 3.71 (s, 2H), 3.41 (s, 2H), 2.99 (m, 1H), 2.30 (s, 3H), 1.24 (d, \(J = 6.6\) Hz, 6H); 
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.9, 144.9, 142.8, 135.1, 132.6, 130.0, 129.0, 128.6, 127.3, 127.2, 126.8, 120.2, 48.8, 47.8, 28.2, 24.1, 20.7; HRMS (ESI): Calc’d for C\(_{20}\)H\(_{23}\)N\(_3\)NaO\(_2^+\), 360.1682; found, 360.1688.
4-(3-Chloro-4-methylphenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (18b)

Compound 18b was isolated in 58% yield (199 mg, red crystal); Mixture of two isomers (ratio: 6 : 1); 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 8.50 (s, 0.2H), 7.30 – 7.18 (m, 2.7H), 7.18 – 7.10 (m, 1.3H), 7.07 (d, $J = 7.5$ Hz, 2H), 6.96 (s, 1H), 6.87 (d, $J = 7.1$ Hz, 0.4H), 6.77 (d, $J = 8.2$ Hz, 1H), 3.68 (s, 2.3H), 3.56 (d, $J = 2.2$ Hz, 2.3H), 2.40 (s, 0.6H), 2.35 (s, 3.5H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 162.2, 146.1, 141.3, 135.4, 135.0, 133.1, 132.7, 131.8, 131.7, 131.6, 131.5, 130.8, 130.7, 130.4, 130.2, 130.1, 130.0, 129.4, 123.1, 120.9, 120.5, 118.8, 118.7, 49.0, 48.6, 44.5, 44.0, 20.8, 20.7, 19.4, 19.2; HRMS (ESI): Calc’d for C$_{18}$H$_{18}$ClN$_3$NaO$_2^+$, 366.0980; found, 366.0975.

4-(2-Fluoro-4-methylphenyl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (16b)

Compound 16b was isolated in 54% yield (177 mg, red crystal); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 7.21 (d, $J = 7.6$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 6.93 (d, $J = 12.5$ Hz, 1H), 6.82 (d, $J = 7.9$ Hz, 1H), 6.73 (t, $J = 8.1$ Hz, 1H), 3.61 (s, 2H), 3.58 (s, 2H), 2.35 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.5 (d, $J = 246.8$ Hz), 141.5, 135.6 (d, $J = 7.4$ Hz), 135.1, 132.2 (d, $J = 9.1$ Hz), 130.4, 129.8, 124.8 (d, $J = 3.1$ Hz), 123.3, 118.7, 117.6 (d, $J = 19.5$ Hz), 48.3, 48.2, 44.3, 20.7 (d, $J = 3.9$ Hz) (one $^{13}$C signal lost for overlap); HRMS (ESI): Calc’d for C$_{18}$H$_{18}$FN$_3$NaO$_2^+$, 350.1275; found, 350.1275.

Ethyl 2-methyl-3-(4-(6-nitro-4-(p-tolyl)-3,4-dihydropyrazin-1(2H)-yl)phenyl) acrylate (25b)

Compound 25b was isolated in 60% yield (244 mg, red crystal); Mixture of two isomers (ratio: 2.7 : 1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.60 (s, 1.4H), 7.63 (s, 0.4H), 7.60 (s, 1H), 7.46 (d, $J = 8.0$ Hz, 0.8H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.21 (m, 2.8H), 7.09 (m, 2.8H), 6.96 (d, $J = 7.7$ Hz, 2H), 6.88 (d, $J = 7.0$ Hz, 0.8H), 4.25 (m, 2.8H), 3.78 (s, 2H), 3.71 (s, 0.8H), 3.59 (s, 2.8H), 2.34 (s, 3H), 2.29 (s, 1H), 2.11 (s, 3.8H), 1.33 (m, 4.2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.8, 168.5, 146.6, 146.3, 141.3, 138.0 (two $^{13}$C), 137.1, 135.5, 133.1 (two $^{13}$C), 132.4, 131.3 (two $^{13}$C), 131.1, 130.5, 130.4, 130.1, 129.3, 129.0, 128.4, 127.3, 120.5, 119.6, 118.8, 117.8, 117.6, 110.0, 109.3, 61.0, 60.8, 49.1, 47.9, 45.1, 43.6, 29.7, 26.9, 20.8, 20.7, 14.3, 14.1 (one $^{13}$C signal lost for overlap); HRMS (ESI): Calc’d for C$_{23}$H$_{25}$N$_3$NaO$_4^+$, 430.1737; found, 430.1738.
4-(Naphthalen-2-yl)-5-nitro-1-(p-tolyl)-1,2,3,4-tetrahydropyrazine (19b)

Compound 19b was isolated in 58% yield (200 mg, red oil); Mixture of two isomers (ratio: 2:1); 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (s, 0.5H), 8.66 (s, 1H), 7.80 (m, 4H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.55 –7.31 (m, 4.5H), 7.28 (d, $J = 8.8$ Hz, 1H), 7.19 (m, 3H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.4$ Hz, 2H), 6.91 (d, $J = 7.2$ Hz, 1H), 3.77 (s, 2H), 3.70 (s, 1H), 3.62 (s, 1H), 3.52 (s, 2H), 2.35 (s, 3H), 2.30 (s, 1.5H); 

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.8, 144.5, 141.4, 141.0, 135.3, 133.9, 133.7, 132.9, 131.1, 130.9, 130.7, 130.4, 130.1 (two $^{13}$C), 130.0, 129.9, 129.8, 129.6, 127.8, 127.6, 127.5, 127.4, 127.1, 126.6, 125.8, 124.7, 120.7, 120.5, 118.8, 117.8, 116.8, 115.8, 49.0, 48.4, 44.5, 44.2, 20.8, 20.7; HRMS (ESI): Calc’d for C$_{21}$H$_{19}$N$_3$NaO$_2^+$, 368.3169; found, 368.1370.

2-Nitro-1,4-di-(p-tolyl)-4,5,6,7-tetrahydro-1H-1,4-diazepine (29b)

Compound 29b was isolated in 48% yield (155 mg, red crystal); 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (s, 1H), 7.19 (d, $J = 7.5$ Hz, 2H), 7.09 (m, 4H), 6.77 (d, $J = 7.9$ Hz, 2H), 4.35 (brs, 1H), 3.82 (brs, 2H), 3.65 (brs, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 2.12 (brs, 2H); 

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.8, 143.3, 139.4, 135.8, 134.0, 130.3, 130.2, 129.4, 120.8, 115.1, 49.3, 49.2, 24.5, 20.8, 20.4; HRMS (ESI): Calc’d for C$_{19}$H$_{21}$N$_3$NaO$_2^+$, 346.1526; found, 346.1522.

N-(2-(Nitroso(p-tolyl)amino)ethyl)-N-(p-tolyl)formamide (26a)

Compound 26a was isolated in 96% yield (285 mg, colorless oil); 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (s, 1H), 7.43 (d, $J = 7.7$ Hz, 2H), 7.25 (d, $J = 7.1$ Hz, 2H), 7.17 (d, $J = 7.6$ Hz, 2H), 6.95 (d, $J = 7.6$ Hz, 2H), 4.25 (t, $J = 6.7$ Hz, 2H), 3.90 (t, $J = 6.7$ Hz, 2H), 2.38 (s, 3H), 2.35 (s, 3H); 

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.6, 139.0, 137.9, 137.5, 137.0, 130.3, 130.1, 123.2, 119.2, 42.0 (two $^{13}$C), 21.0, 20.9; HRMS (ESI): Calc’d for C$_{17}$H$_{19}$N$_3$NaO$_2^+$, 320.1369; found, 320.1364.
$N_1,N_2$-Diethyl-$1$-nitro-$N_1,N_2$-di-$p$-tolylethene-$1,2$-diamine (30b)

Compound 30b was isolated in 45% yield (153 mg, yellow crystal); $^1$H NMR (600 MHz, CDCl$_3$) δ 8.58 (s, 1H), 7.01 (brs, 6H), 6.56 (brs, 2H), 3.84 (s, 2H), 3.37 (brs, 2H), 2.32 (s, 2H), 2.25 (s, 3H), 1.17 (brs, 3H), 1.04 (brs, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.1, 142.1, 136.8, 130.2, 129.7, 128.5, 124.5, 113.4, 45.0, 20.9, 20.4, 14.0, 12.2; HRMS (ESI): Calc’d for C$_{20}$H$_{25}$N$_3$NaO$_2^+$, 362.1839; found, 362.1843.

$1$-(4-Methoxy-2-nitrophenyl)-4-($p$-tolyl)piperazine (6c)

Compound 6c was isolated in 45% yield (147 mg, yellow crystal); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, $J$ = 2.9 Hz, 1H), 7.21 (d, $J$ = 9.0 Hz, 1H), 7.13 – 7.01 (m, 3H), 6.87 (d, $J$ = 8.4 Hz, 2H), 3.81 (s, 3H), 3.31 – 3.21 (m, 4H), 3.18 – 3.09 (m, 4H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.3, 149.2, 145.7, 139.6, 129.7, 129.5, 123.3, 119.8, 116.7, 109.5, 55.9, 52.8, 50.2, 20.4; HRMS (ESI): Calc’d for C$_{18}$H$_{22}$N$_3$O$_3^+$, 328.1656; found, 328.1659.
$^1$H and $^{13}$C spectra

1a
3b