Supporting Information

*tert*-Butyl Peroxybenzoate Mediated Selective and Mild \textit{N}-Benzoylation of Ammonia/Amines under Catalyst- and Solvent-free Conditions

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1. General information:

Materials and Method:

All chemicals and reagents were purchased from S. D. fine chemical, Alfa Aesar, Sigma Aldrich and commercial providers. Solvents were purchased from commercial providers and used without further purification. Reaction was monitor by using Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm, column flow 2 mLmin⁻¹, 80 °C to 240 °C at 10 °C/min rise) was used for the mass analysis of the compounds. Products were purified by column chromatography on silica (100-200 mesh). The ¹H NMR spectrum was recorded on Bruker-400 MHz and Bruker-500 MHz spectrometer in CDCl₃ using tetramethylsilane (TMS) as an internal standard. The ¹³C NMR spectrum was recorded on Bruker-100 MHz and Bruker-125 MHz spectrometer in CDCl₃. Chemical shift is reported in parts per million (δ) relative to tetramethylsilane as an internal standard. J (coupling constant) value was reported in Hz. Splitting patterns of proton are illustrated as s (singlet), d (doublet), t (triplet) and m (multiplet). The identities of compounds were confirmed by the comparison of their ¹H and ¹³C NMR spectra with those of authentic data.

2. General experimental procedure for the synthesis of amide from ammonia/amine and TBPB:

A mixture of TBPB (1 mmol) and suitable aqua ammonia/amine (1.1 mmol) were charged in a round bottom flask. The reaction mixture was stirred at room temperature for the indicated time and progress of the reaction was monitored by TLC/GC. The crude product was directly purified by column chromatography (silica gel, 100-200 mesh, PE–EtOAc) to provide the desired pure product. The identity of the compound was confirmed by ¹H and ¹³C NMR spectroscopic methods.
3. Spectral data of compounds:

\( \text{N-(4-methoxybenzyl)benzamide (3c)} \)

\[ \text{3c} \]

\({^1}\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.77 \text{ (d, } J = 7.1 \text{ Hz, 2H), } 7.48 \text{ (t, } J = 7.2 \text{ Hz, 1H), } 7.41 \text{ (t, } J = 7.7 \text{ Hz, 2H), } 7.27 \text{ (d, } J = 8.5 \text{ Hz, 2H), } 6.87 \text{ (d, } J = 8.6 \text{ Hz, 2H), } 6.45 \text{ (br, s, 1H), } 4.56 \text{ (d, } J = 5.56 \text{ Hz, 2H), } 3.79 \text{ (s, 3H ppm); } \text{C NMR (100 MHz, CDCl}_3\text{): } \delta 167.29, 159.11, 134.43, 131.50, 130.25, 129.31, 128.57, 126.95, 114.15, 55.31, 43.63 \text{ ppm.} \]

\( \text{N-(4-fluorobenzyl)benzamide (3e)} \)

\[ \text{3e} \]

\({^1}\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.78 \text{ (d, } J = 8.0 \text{ Hz, 2H), } 7.49 \text{ (t, } J = 7.3 \text{ Hz, 1H), } 7.40 \text{ (t, } J = 7.7 \text{ Hz, 2H), } 7.31-7.25 \text{ (m, 2H), } 7.0 \text{ (t, } J = 8.6 \text{ Hz, 2H), } 6.67 \text{ (br, s, 1H), } 4.58 \text{ (d, } J = 5.58 \text{ Hz, 2H ppm; } \text{C NMR (100 MHz, CDCl}_3\text{): } \delta 167.45, 162.2 \text{ (d, } J_{C:F} = 244 \text{ Hz), } 134.21, 134.07, 131.64, 129.53 \text{ (d, } J_{C:F} = 8 \text{ Hz), } 128.60, 126.98, 115.56 \text{ (d, } J_{C:F} = 21 \text{ Hz), } 43.33 \text{ ppm.} \]

\( \text{N-(3-chlorobenzyl)benzamide (3f)} \)

\[ \text{3f} \]

\({^1}\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.78 \text{ (d, } J = 7.16 \text{ Hz, 2H), } 7.49 \text{ (t, } J = 8.4 \text{ Hz, 1H), } 7.41 \text{ (t, } J = 7.7 \text{ Hz, 2H), } 7.30 \text{ (s, 1H), } 7.25-7.18 \text{ (m, 3H), } 6.77 \text{ (br, s, 1H), } 4.58 \text{ (d, } J = 5.72 \text{ Hz, 2H ppm; } \text{C NMR (100 MHz, CDCl}_3\text{): } \delta 167.54, 140.34, 134.52, 134.04, 131.71, 129.99, 128.62, 127.80, 127.68, 127.01, 125.89, 43.42 \text{ ppm.} \]

\( \text{N-(4-cyanobenzyl)benzamide (3g)} \)

\[ \text{3g} \]
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.80 (d, $J = 7.9$ Hz, 2H), 7.59 (d, $J = 6.6$ Hz, 2H), 7.52 (t, $J = 7.3$Hz, 1H), 7.45-7.41 (m, 4H), 6.89 (br, s, 1H), 4.67 (d, $J = 6.0$ Hz, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.67, 143.96, 133.76, 132.47, 131.93, 128.70, 128.19, 127.02, 118.73, 111.21, 43.48 ppm.

$N$-(1-phenylethyl)benzamide (3h)$^3$

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\text{\begin{tabular}{c}
\text{\textbf{3h}}
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$^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (d, $J = 7.1$ Hz, 2H), 7.49-7.45 (m, 1H), 7.41-7.33 (m, 6H), 7.29-7.25 (m, 1H), 6.44 (d, $J = 6.7$ Hz, 1H), 5.34-5.31 (m, 1H), 1.59 (d, $J = 6.92$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.62, 143.16, 134.60, 131.48, 128.76, 128.57, 127.47, 126.96, 126.28, 49.23, 21.75 ppm.

$N$-(pyridin-2-ylmethyl)benzamide (3i)$^2$

\[
\text{\begin{tabular}{c}
\text{\textbf{3i}}
\end{tabular}}
\]

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.55 (d, $J = 4.8$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.71 (s, br, 1H), 7.69-7.65 (m, 1H), 7.52-7.50 (m, 1H), 7.49-7.42 (m, 2H), 7.41-7.32 (m, 1H), 7.23-7.19 (m, 1H), 4.75 (d, $J = 4.9$ Hz, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.45, 156.29, 148.98, 136.91, 134.32, 131.51, 128.55, 127.11, 122.47, 122.29, 44.76 ppm.

$N$-(pyridin-3-ylmethyl)benzamide (3j)$^3$

\[
\text{\begin{tabular}{c}
\text{\textbf{3j}}
\end{tabular}}
\]

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.49 (s, 1H), 8.45 (d, $J = 4.8$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.50-7.46 (m, 1H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.32 (s, br, 1H),
7.24-7.21 (m, 1H), 4.59 (d, J = 5.96, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.78, 149.03, 148.68, 135.81, 134.24, 133.96, 131.74, 128.59, 127.09, 123.68, 41.40 ppm.

$N$-(pyridin-4-ylmethyl)benzamide (3k)$^{2}$

\[ \text{3k} \]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.47 (d, J = 5.2 Hz, 2H), 7.82 (d, J = 7.5 Hz, 2H), 7.52-7.49 (m, 1H), 7.40 (t, J = 7.8 Hz, 2 H), 7.35 (s, br, 1 H), 7.19 (d, J = 5.6, 2H), 4.59 (d, J = 6.0 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.88, 149.90, 147.69, 133.85, 131.87, 128.66, 127.10, 122.30, 42.72 ppm.

$N$-cyclohexylbenzamide (3t)$^{4}$

\[ \text{3t} \]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (d, J = 8.0 Hz, 2H), 7.49-7.38 (m, 3H), 6.07 (s, br, 1H), 3.99-3.95 (m, 1H), 2.04-2.00 (m, 2H), 1.77-1.62 (m, 3H), 1.46-1.21 (m, 5H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.67, 135.10, 131.23, 128.50, 126.85, 48.69, 33.23, 25.58, 24.94 ppm.

$N$-(2-aminobenzyl)benzamide (6a)$^{6}$

\[ \text{6a} \]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (d, J = 7.12 Hz, 2H), 7.49-7.45 (m, 1H), 7.41-7.36 (m, 2H), 7.10 (d, J = 7.3 Hz, 2H), 6.70-6.64 (m, 2H), 6.56 (s, br, 1H), 4.56 (d, J = 6.1 Hz, 2H), 3.99 (s, br, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.88, 145.67, 133.97, 131.66, 130.68, 129.33, 128.58, 126.98, 121.73, 117.81, 115.80, 41.36 ppm.
$N$-(3-aminobenzyl)benzamide (6b)$^3$

\[
\begin{array}{c}
\text{N} \quad \text{O} \\
\text{H} \quad \text{N} \\
\text{H} \quad \text{NH}_2
\end{array}
\]

$6b$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 7.08$ Hz, 2H), 7.51-7.47 (m, 1H), 7.43-7.39 (m, 2H), 7.12 (t, $J = 7.7$ Hz, 1H), 6.71 (d, $J = 7.6$ Hz, 1H), 6.66 (s, 1 H), 6.60 (d, $J = 8$ Hz, 1H), 6.46 (s, br, 1 H), 4.53 (d, $J = 5.6$ Hz, 2H), 3.70 (s, br, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.34, 146.90, 139.38, 134.41, 131.54, 129.75, 128.60, 126.98, 117.98, 114.47, 114.37, 44.18 ppm.

$N$-(4-aminobenzyl)benzamide (6c)$^5$

\[
\begin{array}{c}
\text{N} \quad \text{O} \\
\text{H} \quad \text{N} \\
\text{H} \quad \text{NH}_2
\end{array}
\]

$6c$

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.76 (d, $J = 8.5$ Hz, 2H), 7.49-7.46 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.67 (d, $J = 8.5$ Hz, 2H), 6.28 (s, br, 1 H), 4.52 (d, $J = 5.0$ Hz, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.21, 145.98, 134.56, 131.41, 129.31, 128.53, 127.89, 126.90, 115.27, 43.86 ppm.

4. References:


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

N-(4-methoxybenzyl)benzamide (3c) $^1$H NMR
$N$-(4-methoxybenzyl)benzamide (3c) $^{13}$C NMR
$N$-(4-fluorobenzyl)benzamide (3e) $^1$H NMR
$N$-(4-fluorobenzyl)benzamide (3e) $^{13}$C NMR
$N$-(3-chlorobenzyl)benzamide (3f) $^1$H NMR
N-(3-chlorobenzyl)benzamide (3f) $^{13}$C NMR
$N$-(4-cyanobenzyl)benzamide (3g) $^1$H NMR
\textit{N-(4-cyanobenzyl)benzamide (3g) $^{13}\text{C}$ NMR}
N-(1-phenylethyl)benzamide (3h) $^1$H NMR
$N$-(1-phenylethyl)benzamide (3h) $^{13}$C NMR

![N-(1-phenylethyl)benzamide (3h) $^{13}$C NMR](image)
$N$-(pyridin-2-ylmethyl)benzamide (3i) $^1$H NMR

\[
\begin{align*}
&\text{Chemical Structure:} \\
&\text{NMR Spectrum:}
\end{align*}
\]
$N$-(pyridin-2-ylmethyl)benzamide (3i) $^{13}$C NMR

![N-(pyridin-2-ylmethyl)benzamide (3i) $^{13}$C NMR spectrum](image-url)
N-(pyridin-3-ylmethyl)benzamide (3j) $^1$H NMR
$N$-(pyridin-3-ylmethyl)benzamide (3j) $^{13}$C NMR
N-(pyridin-4-ylmethyl)benzamide (3k) $^1$H NMR
$N$-(pyridin-4-ylmethyl)benzamide (3k) $^{13}$C NMR
N-cyclohexylbenzamide (3t) $^1$H NMR
$N$-cyclohexylbenzamide (3t) $^{13}$C NMR
$N$-(2-aminobenzyl)benzamide (6a) $^1$H NMR
N-(2-aminobenzyl)benzamide (6a) $^{13}$C NMR
N-(3-aminobenzyl)benzamide (6b) $^1$H NMR
$N$-(3-aminobenzyl)benzamide (6b) $^{13}$C NMR
$N$-(4-aminobenzyl)benzamide (6c) $^1$H NMR
N-(4-aminobenzyl)benzamide (6c) $^{13}$C NMR