Base-mediated formation of amides from aliphatic amines and ynones as acylation agents via C–C bond cleavage at room temperature

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All reagents were used directly without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. $^1$H and $^{13}$C NMR spectra were measured on a 400 MHz Bruker spectrometer ($^1$H 400 MHz, $^{13}$C 100 MHz), using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. HRMS-ESI spectra were obtained on Agilent 6450 spectrometer. The products listed below were determined by $^1$H, $^{13}$C NMR. PE is petroleum ether (60–90 °C).
2. General Procedure for Synthesis of 3a-l, 4a-u.

\[
\begin{align*}
R^1\text{NH}_2 & + R^2\text{CO}_\text{Ph} & \xrightarrow{\text{LiO}Bu (1.2 \text{ equiv})} & R^1\text{N}R^2 \\
1 & & \text{DCM, rt, 2-6 h} & 3, 4
\end{align*}
\]

LiO\text{Bu} (20 mg, 0.24 mmol) was added to a solution of amines 1 (0.2 mmol) in dry dichloromethane (1.0 mL). The solution was stirred for 5 min at room temperature, then ynones 2 (0.24 mmol) was added. The solution was stirred for another 2-6 h at room temperature. After the reaction finished, the organic layer was washed with saturated aqueous sodium chloride (2.0 mL), dried over sodium sulfate, filtered and concentrated. The residue was purified by column chromatography (ethyl acetate/PE = 1/4) to yield the desired amides. Note: in the case of 4q, ynones 2a (0.48 mmol) was used.

\[\text{N-benzylbenzamide (3a)}^1\]

Substrate 3a was obtained as white powder (34.6 mg, 82%); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta \) 7.78 (d, \(J = 7.6 \text{ Hz, 2H}), 7.48 \text{ t, } J = 7.3 \text{ Hz, 1H), 7.40 (t, } J = 7.6 \text{ Hz, 2H), 7.37 – 7.24 \text{ (m, 5H), 6.58 (s, 1H), 4.62 (d, } J = 5.7 \text{ Hz, 2H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta \) 167.3, 138.2, 134.3, 131.5, 128.7, 128.5, 127.8, 127.5, 126.9, 44.1.

\[\text{N-benzyl-2-methylbenzamide (3b)}^1\]

Substrate 3b was obtained as white powder (22.5 mg, 50%); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta \) 7.40 – 7.25 (m, 7H), 7.22 – 7.15 (m, 2H), 6.08 (s, 1H), 4.61 (d, \(J = 5.7 \text{ Hz, 2H), 2.46 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta \) 169.9, 138.2, 136.2, 136.2, 131.0, 129.9, 128.8, 127.8, 127.6, 126.6, 125.7, 43.9, 19.8.

\[\text{N-benzyl-2-methoxybenzamide (3c)}^2\]

Substrate 3c was obtained as white powder (34.3 mg, 71%); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta \) 8.30 – 8.22 (m, 1H), 8.19 (s, 1H), 7.45 (t, \(J = 7.8 \text{ Hz, 1H), 7.41 – 7.23 \text{ (m, 5H), 7.09 (t, } J = 7.6 \text{ Hz, 1H), 6.96 (d, } J = 8.3 \text{ Hz, 1H), 4.69 (d, } J = 5.7 \text{ Hz, 2H), 3.91 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta \) 165.3, 157.5, 138.8, 132.8, 132.4, 128.6, 127.5, 127.2, 121.4, 121.2, 111.3, 55.9, 43.7.

\[\text{N-benzyl-2-bromoxbenzamide (3d)}^3\]

Substrate 3d was obtained as white powder (34.8 mg, 60%); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta \) 7.57 (td, \(J = 7.8, 7.7, 1.5 \text{ Hz, 2H), 7.43 – 7.24 \text{ (m, 7H), 6.25 (s, 1H), 4.66 (d, } J = 5.6 \text{ Hz, 2H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta \) 167.4, 137.6, 137.6, 133.4, 131.3, 129.6, 128.8, 128.0, 127.7, 127.6, 119.3, 44.3.
**N-benzyl-3-methoxybenzamide (3e)**

Substrate 3e was obtained as white powder (41.0 mg, 85%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.35 (m, 1H), 7.33 – 7.19 (m, 7H), 7.03 (brs, 1H), 6.99 – 6.94 (m, 1H), 4.53 (d, $J$ = 5.6 Hz, 2H), 3.74 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 159.6, 138.2, 135.7, 129.3, 128.5, 127.6, 127.2, 118.8, 117.5, 112.3, 55.2, 43.8.

**N-benzyl-4-methylbenzamide (3f)**

Substrate 3f was obtained as white powder (35.6 mg, 79%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J$ = 8.0 Hz, 2H), 7.39 – 7.24 (m, 5H), 7.21 (d, $J$ = 7.9 Hz, 2H), 6.46 (d, $J$ = 5.6 Hz, 2H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 141.9, 138.3, 131.5, 129.2, 128.7, 127.9, 127.5, 126.9, 44.0, 21.4.

**N-benzyl-4-(tert-butyl)benzamide (3g)**

Substrate 3g was obtained as white powder (41.7 mg, 78%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J$ = 8.3 Hz, 2H), 7.43 (d, $J$ = 8.3 Hz, 2H), 7.39 – 7.24 (m, 5H), 6.50 (s, 1H), 4.63 (d, $J$ = 5.7 Hz, 2H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 155.0, 138.4, 128.7, 127.8, 127.5, 126.8, 125.5, 44.0, 34.9, 31.1.

**N-benzyl-4-methoxybenzamide (3h)**

Substrate 3h was obtained as white powder (40.5 mg, 84%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 8.7 Hz, 2H), 7.40 – 7.24 (m, 5H), 6.91 (d, $J$ = 8.8 Hz, 2H), 6.37 (s, 1H), 4.62 (d, $J$ = 5.7 Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.8, 162.2, 138.4, 128.7, 127.9, 127.5, 126.7, 113.7, 55.4, 44.1.

**N-benzyl-4-fluorobenzamide (3i)**

Substrate 3i was obtained as white powder (34.3 mg, 75%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.74 (m, 2H), 7.40 – 7.24 (m, 5H), 7.17 – 6.99 (m, 2H), 6.41 (s, 1H), 4.62 (d, $J$ = 5.7 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.26, 164.7 (d, $J$ = 252.0 Hz), 138.0, 130.5, 129.3 (d, $J$ = 8.9 Hz), 128.8, 127.9, 127.7, 115.6 (d, $J$ = 21.9 Hz), 44.2.

**N-benzyl-4-chlorobenzamide (3j)**
Substrate 3j was obtained as white powder (37.8 mg, 77%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.6$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 2H), 7.37 – 7.27 (m, 5H), 6.42 (s, 1H), 4.62 (d, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.2, 137.9, 137.8, 132.7, 128.8, 128.4, 127.9, 127.7, 44.2.

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\text{H} \\
\text{N} \\
\text{S} \\
\text{2}\end{array}
\]

$N$-benzylthiophene-2-carboxamide (3k)$^8$

Substrate 3k was obtained as white powder (34.8 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (dd, $J = 3.7$, 1.1 Hz, 1H), 7.47 (dd, $J = 5.0$, 1.1 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.08 – 7.03 (m, 1H), 6.39 (s, 1H), 4.61 (d, $J = 5.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.8, 138.7, 138.0, 130.0, 128.7, 128.1, 127.9, 126.6, 44.0.

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\text{H} \\
\text{N} \\
\text{O} \\
\text{S} \\
\text{2}\end{array}
\]

$N$-benzylationacetamide (3l)$^9$

Substrate 3l was obtained as white powder (7.5 mg, 25%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.23 (m, 5H), 5.82 (s, 1H), 4.42 (d, $J = 5.7$ Hz, 2H), 2.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.8, 138.2, 128.7, 127.8, 127.5, 43.8, 23.3.

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\text{H} \\
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\text{Me} \\
\text{2}\end{array}
\]

$N-(3$-bromobenzyl)$benzamide$ (4a)$^{10}$

Substrate 4a was obtained as white powder (43.5 mg, 75%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 – 7.74 (m, 2H), 7.55 – 7.45 (m, 2H), 7.45 – 7.36 (m, 3H), 7.31 – 7.23 (m, 1H), 7.19 (t, $J = 7.7$ Hz, 1H), 6.63 (s, 1H), 4.59 (d, $J = 5.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 140.6, 134.1 131.7, 130.7, 130.6, 128.6, 127.0, 126.4, 44.3.

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\begin{array}{c}
\text{H} \\
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\text{Br} \\
\text{2}\end{array}
\]

$N$-(4-methylbenzyl)$benzamide$ (4b)$^8$

Substrate 4b was obtained as white powder (40.6 mg, 90%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 – 7.74 (m, 2H), 7.52 – 7.45 (m, 1H), 7.42 – 7.38 (m, 2H), 7.27 – 7.21 (m, 2H), 7.15 (d, $J = 7.8$ Hz, 2H), 6.45 (s, 1H), 4.59 (d, $J = 5.5$ Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 137.3, 135.1, 134.4, 131.4, 129.4, 128.5, 127.9, 126.9, 43.9, 23.3.

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\begin{array}{c}
\text{H} \\
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\text{Me} \\
\text{2}\end{array}
\]

$N$-(4-(tert-butyld)benzyl)$benzamide$ (4c)$^{11}$

Substrate 4c was obtained as white powder (48.7 mg, 91%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 – 7.75 (m, 2H), 7.52 – 7.45 (m, 1H), 7.45 – 7.33 (m, 4H), 7.29 (d, $J = 8.2$ Hz, 2H), 6.48 (s, 1H), 4.60 (d, $J = 5.5$ Hz, 2H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 150.6, 135.1, 134.5, 131.4, 128.5, 127.7, 126.9, 125.7, 43.8, 34.5, 31.3.

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\text{H} \\
\text{N} \\
\text{tBu} \\
\text{2}\end{array}
\]
**N-(4-aminobenzyl)benzamide (4d)**

Substrate 4d was obtained as gray powder (36.7 mg, 86%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 – 7.72 (m, 2H), 7.51 – 7.43 (m, 1H), 7.39 (t, $J$ = 8.3 Hz, 2H), 7.13 (d, $J$ = 8.4 Hz, 2H), 6.64 (d, $J$ = 8.3 Hz, 2H), 6.40 (s, 1H), 4.50 (d, $J$ = 5.4 Hz, 2H), 3.57 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 145.9, 134.5, 131.3, 129.2, 128.5, 127.9, 126.9, 115.2, 43.8.

**N-(3,4-dimethoxybenzyl)benzamide (4e)**

Substrate 4e was obtained as white powder (44.0 mg, 81%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J$ = 7.4 Hz, 2H), 7.50 – 7.40 (m, 1H), 7.40 – 7.31 (m, 2H), 7.03 (s, 1H), 6.84 (d, $J$ = 6.1 Hz, 2H), 6.76 (dd, $J$ = 8.6, 1.9 Hz, 1H), 4.51 (d, $J$ = 5.6 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 148.9, 148.2, 134.2, 131.2, 130.8, 128.3, 126.8, 119.9, 111.1, 111.1, 55.7, 55.6, 43.6; HRMS m/z (ESI) calcd for C$_{16}$H$_{18}$NO$_3$ (M + H)$^+$ 272.1281, found 272.1286.

**N-(4-chlorobenzyl)benzamide (4f)**

Substrate 4f was obtained as white powder (39.3 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J$ = 7.6 Hz, 2H), 7.50 – 7.40 (m, 1H), 7.40 – 7.31 (m, 2H), 7.03 (s, 1H), 6.84 (d, $J$ = 6.1 Hz, 2H), 6.76 (dd, $J$ = 8.6, 1.9 Hz, 1H), 4.51 (d, $J$ = 5.6 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 136.8, 134.1, 133.3, 131.6, 129.1, 128.6, 126.9, 43.3.

**N-(4-trifluoromethylbenzyl)benzamide (4g)**

Substrate 4g was obtained as white powder (44.7 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J$ = 7.6 Hz, 2H), 7.58 (d, $J$ = 7.9 Hz, 2H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.41 (t, $J$ = 7.7 Hz, 2H), 7.34 – 7.21 (m, 4H), 6.61 (s, 1H), 4.68 (d, $J$ = 5.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.5, 142.4, 134.0, 131.8, 129.8 (q, $J$ = 32.8, 32.0 Hz), 128.6, 127.9, 127.0, 125.6 (q, $J$ = 3.6 Hz), 124.0 (q, $J$ = 272.4 Hz), 43.5.

**N-(naphthalen-1-ylmethyl)benzamide (4h)**

Substrate 4h was obtained as white powder (41.8 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 – 8.04 (m, 1H), 7.89 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.80 – 7.71 (m, 2H), 7.58 – 7.34 (m, 7H), 6.37 (s, 1H), 5.09 (d, $J$ = 5.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 134.3, 133.9, 133.4, 131.5, 131.5, 128.8, 128.8, 128.5, 128.5, 126.9, 126.8, 126.0, 125.4, 123.5, 42.4.

**N-(thiophen-2-ylmethyl)benzamide (4i)**
Substrate 4i was obtained as white powder (26.1 mg, 60%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 – 7.73 (m, 2H), 7.50 – 7.42 (m, 1H), 7.41 – 7.33 (m, 2H), 7.20 (dd, $J$ = 5.1, 1.2 Hz, 1H), 6.99 (dt, $J$ = 3.2, 1.0, 1.0 Hz, 1H), 6.93 (dd, $J$ = 5.1, 3.4 Hz, 1H), 6.85 (s, 1H), 4.76 (d, $J$ = 5.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 140.8, 134.0, 131.5, 128.4, 127.0, 126.8, 126.0, 125.1, 38.7.

$N$-(2-(pyridin-2-yl)ethyl)benzamide (4j)$^{13}$

Substrate 4j was obtained as white powder (38.0 mg, 84%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J$ = 3.1 Hz, 1H), 7.78 (d, $J$ = 7.2 Hz, 2H), 7.72 (s, 1H), 7.60 (td, $J$ = 7.7, 7.6, 1.9 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.38 (dd, $J$ = 8.2, 6.5 Hz, 2H), 7.16 (m, 2H), 3.83 (q, $J$ = 6.1, 6.1, 6.1 Hz, 2H), 3.08 (t, $J$ = 6.3, 6.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 159.6, 148.9, 136.6, 134.5, 131.1, 128.3, 123.4, 121.5, 39.2, 36.5.

$N$-(2-bromophenethyl)benzamide (4k)$^{14}$

Substrate 4k was obtained as white powder (48.0 mg, 79%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J$ = 3.1 Hz, 1H), 7.78 (d, $J$ = 7.2 Hz, 2H), 7.72 (s, 1H), 7.60 (td, $J$ = 7.7, 7.6, 1.9 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.38 (dd, $J$ = 8.2, 6.5 Hz, 2H), 7.23 – 7.10 (m, 2H), 3.83 (q, $J$ = 6.1, 6.1, 6.1 Hz, 2H), 3.08 (t, $J$ = 6.3, 6.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.6, 138.3, 134.5, 133.0, 131.4, 131.1, 128.5, 128.3, 127.7, 126.8, 124.6, 39.8, 35.7.

$N$-butylbenzamide (4l)$^{15}$

Substrate 4l was obtained as white powder (30.4 mg, 86%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.72 (m, 2H), 7.52 – 7.43 (m, 1H), 7.43 – 7.36 (m, 2H), 6.35 (s, 1H), 3.51 – 3.38 (m, 2H), 1.65 – 1.54 (m, 2H), 1.45 – 1.35 (m, 2H), 0.95 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.5, 134.8, 131.2, 128.4, 126.8, 39.8, 31.7, 20.1, 13.7.

$N$-allylbenzamide (4m)$^{16}$

Substrate 4m was obtained as white powder (27.7 mg, 86%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 – 7.75 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.35 (m, 2H), 6.69 (s, 1H), 5.91 (ddt, $J$ = 17.2, 10.2, 5.6, 5.6 Hz, 1H), 5.30 – 5.11 (m, 2H), 4.05 (tt, $J$ = 5.7, 5.7, 1.6, 1.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 134.3, 134.1, 131.3, 128.4, 126.9, 116.4, 42.3.

$N$-isopropylbenzamide (4n)$^{15}$

Substrate 4n was obtained as white powder (23.5 mg, 72%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 – 7.71 (m, 2H), 7.52 – 7.45 (m, 1H), 7.41 (t, $J$ = 7.3 Hz, 2H), 5.95 (s, 1H), 4.42 – 4.20 (m, 1H), 1.26 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 135.0, 131.2, 128.5, 126.8, 41.9, 22.8.
Substrate 4o was obtained as white powder (27.0 mg, 60%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 7.3 Hz, 2H), 7.48 (t, $J$ = 7.3 Hz, 1H), 7.42 – 7.32 (m, 6H), 7.31 – 7.23 (m, 1H), 6.40 (s, 1H), 5.37 – 5.28 (m, 1H), 1.60 (d, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.5, 143.1, 134.6, 131.4, 128.7, 128.5, 127.4, 126.9, 126.2, 49.2, 21.7.

Substrate 4p was obtained as white powder (28.9 mg, 71%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 7.8 Hz, 2H), 7.48 (t, $J$ = 7.5 Hz, 2H), 5.98 (s, 1H), 4.06 – 3.92 (m, 1H), 2.06 – 2.01 (m, 2H), 1.79 – 1.72 (m, 2H), 1.67 – 1.63 (m, 1H), 1.56 – 1.36 (m, 2H), 1.37 – 1.11 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 135.1, 131.2, 128.5, 126.8, 48.6, 33.2, 25.6, 24.9.

Substrate 4q was obtained as white powder (31.1 mg, 55%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 – 7.76 (m, 4H), 7.52 – 7.44 (m, 2H), 7.44 – 7.32 (m, 5H), 7.12 (d, $J$ = 7.3 Hz, 1H), 4.42 – 4.33 (m, 1H), 3.74 – 3.65 (m, 1H), 1.31 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 168.2, 134.0, 133.9, 131.6, 131.5, 128.5, 128.5, 127.01, 127.00, 47.2, 46.5, 18.4.

Substrate 4s was obtained as colorless oil (32.8 mg, 73%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.25 (m, 9H), 7.16 (s, 1H), 4.76 (s, 1H), 4.51 (s, 1H), 3.03 (s, 1.5H), 2.85 (s, 1.5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.2, 171.5, 136.9, 136.5, 136.1, 132.7, 129.8, 129.5, 128.6, 128.3, 128.1, 128.1, 127.5, 126.9, 126.7, 55.1, 50.7, 36.9, 33.1.

Substrate 4t was obtained as colorless oil (19.3 mg, 55%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 – 7.47 (m, 2H), 7.43 – 7.35 (m, 3H), 3.64 (t, 7.0 Hz, 2H), 3.42 (t, 6.6 Hz, 2H), 1.99 – 1.81 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.6, 137.1, 129.6, 128.1, 126.9, 49.4, 46.0, 26.2, 24.3.
**tert-butyl (3-(benzamidomethyl)phenyl)carbamate (5a)**

Substrate 5a was obtained as white powder (56.1 mg, 86%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 – 7.76 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.36 (m, 3H), 7.27 (dd, $J$ = 10.9, 4.9 Hz, 2H), 7.06 – 6.99 (m, 1H), 6.63 (s, 1H), 6.58 (s, 1H), 4.58 (d, $J$ = 5.7 Hz, 2H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.36, 152.76, 139.13, 138.76, 134.29, 131.51, 129.37, 128.54, 126.98, 122.48, 117.97, 117.75, 80.60, 44.02, 28.29; HRMS m/z (ESI) calcd for C$_{19}$H$_{23}$N$_2$O$_3$ (M + H)$^+$ 327.1703, found 327.1709.

![Ac-NH-O](image)

**N-(3-acetamidobenzyl)benzamide (5b)**

Substrate 5b was obtained as white powder (45.5 mg, 84%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (s, 1H), 7.82 – 7.74 (m, 2H), 7.51 – 7.32 (m, 5H), 7.23 – 7.14 (m, 1H), 7.08 – 6.96 (m, 2H), 4.48 (s, 2H), 2.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.2, 167.8, 138.9, 138.5, 134.0, 131.5, 129.1, 128.5, 127.0, 123.1, 119.2, 119.2, 43.7, 24.2; HRMS m/z (ESI) calcd for C$_{16}$H$_{17}$N$_2$O$_2$ (M + H)$^+$ 269.1285, found 269.1289.

**Reference:**

3. $^1$H and $^{13}$C NMR Spectra

![NMR Spectra](image)

3a
3c

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

3c

\[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{H} \\
\text{O}
\end{array} \]
\[
\text{NMe}
\]

- [Chemical structure](image)

- 

- [NMR spectrum](image)

- [Chemical structure](image)
4e