SUPPORTING INFORMATION

Significance of reagent addition sequence in the amidation of carboxylic acids mediated by PPh$_3$ and I$_2$

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Materials and methods

All reagents and polymer-supported triphenylphosphine (PS-PPh3, 3.0 mmol/g, 2% DVB) were purchased from Sigma-Aldrich Co., USA, and were used without further purification. The reaction was monitored by thin-layer chromatography carried out on silica gel plates (60F254, MERCK, Germany) and visualized under UV light (245 nm). Column chromatography was performed over silica gel 60 (70–230 mesh, MERCK, Germany). Melting points were determined using SANYO, Gallenkamp apparatus at a heating rate of 10 °C/min and were uncorrected. NMR measurements were recorded on a Bruker AVANCE™ (400 MHz for 1H) using chloroform-d (CDCl3) as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in parts per million (ppm, δ) downfield from TMS. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublet (dd), and triplet of doublet (td). High Resolution Mass Spectrometry (HRMS) was performed with a MicroTOF LC, Bruker Daltonics.
Investigation toward the synthesis of N-benzylbenzamide using PPh$_3$-I$_2$ (Method A)

To a stirred solution of iodine (0.49 mmol) in CH$_2$Cl$_2$ was added with one portion of PPh$_3$ (0.49 mmol) at 0°C. Benzoic acid (0.41 mmol) was then added, and continuously stirred for 5 min. Subsequently, this resulting mixture was treated with triethylamine (0.82 mmol) and stirred for 5 min, followed by addition of benzylamine (0.49 mmol). The solution was allowed to warm up to room temperature and stirred for further 10 min. The crude mixture was concentrated under reduced pressure, then purified by column chromatography using 10% ethyl acetate in hexane.

\[
\begin{align*}
\text{O} &\quad \text{O} \\
\text{C} &\quad \text{C}
\end{align*}
\]

**Benzoic anhydride:** Following the above procedure, the product was obtained as a colorless oil (0.0455 g, 98% yield); $R_f$ 0.40 (10% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.40 (dd, $J = 8.4$, 1.2 Hz, 4H), 7.70 (td, $J = 8.4$, 1.2 Hz, 2H), 7.55 (td, $J = 8.4$, 1.2 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.4, 134.6, 130.6, 128.92, 128.85.
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
Investigation toward the synthesis of N-benzylbenzamide using PPh₃-I₂ (Method B)

To a stirred solution of iodine (0.49 mmol) in CH₂Cl₂ (2 mL) was added with one portion of Ph₃P (0.49 mmol) at 0°C. Benzylamine (0.49 mmol) was added with continuously stirring for 5 min. The resulting mixture was then treated with triethylamine (0.82 mmol), followed by addition of benzoic acid (0.41 mmol). After the solution was allowed to warm up to room temperature and stirred for 10 min, the crude mixture was concentrated under reduced pressure, then purified by column chromatography using 60% ethyl acetate in hexane.

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\text{(Benzylamino)triphenylphosphonium iodide: Following the above procedure, (benzylamino)triphenylphosphonium iodide was obtained as a molten yellow solid (0.2427 g, 98% yield); } R_f 0.27 (100% EtOAc); ^{31}\text{P}\{\text{H}\} \text{ NMR (162 MHz, CDCl}_3\text{): } \delta 39.17 \text{ (s); } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.79-7.73 \text{ (m, 9H), 7.62-7.57 (m, 6H), 7.17-7.12 (m, 5H), 4.29 (d, } J = 7.6\text{Hz, 1H) , 4.25 (d, } J = 7.6\text{Hz, 1H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 138.00, 137.97, 134.98, 134.95, 133.70, 133.59, 130.0, 129.8, 128.4, 128.1, 127.5, 121.4, 120.4, 45.2; \text{ HRMS-ESI (m/z): [M]+ calcd for C}_{25}\text{H}_{23}\text{NP}^+, 368.1563; \text{ found, 368.1585.}}
\]
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$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
Investigation toward the synthesis of N-benzylbenzamide using PPh$_3$-I$_2$ (Method C)
To a stirred solution of iodine (0.49 mmol) in CH$_2$Cl$_2$ (2 mL) was added with one portion of Ph$_3$P (0.49 mmol) at 0°C. This resulting mixture was added with benzoic acid (0.41 mmol) and stirred for 30 min. Benzylamine (0.49 mmol) was added with continuously stirring for 5 min, followed by addition of triethylamine (0.82 mmol). After the solution was allowed to warm up to room temperature and stirred for further 10 min, the crude mixture was concentrated under reduced pressure then purified by column chromatography using 10-40% ethyl acetate in hexane to give N-benzylbenzamide (0.0824 g, 95% yield).

Investigation toward the synthesis of N-benzylbenzamide using PPh$_3$-I$_2$ (Method D)
To a stirred solution of iodine (0.49 mmol) in CH$_2$Cl$_2$ (2 mL) was added with one portion of Ph$_3$P (0.49 mmol) at 0°C. Benzylamine (0.49 mmol) was added with continuously stirring for 5 min. Subsequently, this resulting mixture was treated with benzoic acid (0.41 mmol) and stirred for 5 min, followed by addition of triethylamine (0.82 mmol). After the solution was allowed to warm up to room temperature and stirred for 10 min, the crude mixture was concentrated under reduced pressure then purified by column chromatography using 10-40% ethyl acetate in hexane to give N-benzylbenzamide (0.0856 g, 99% yield).

**N-Benzylbenzamide** (Table 1, entry 1): Following the general procedure and purification by column chromatography, N-benzylbenzamide was obtained as a white solid (0.0856 g, 99% yield); mp 104-105 °C; $R_f$ 0.37 (30% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J$ = 7.2 Hz, 2H); 7.47 (t, $J$ = 7.2 Hz, 2H), 7.38 (t, $J$ = 7.2 Hz, 2H), 7.32-7.25 (m, 5H), 7.03 (br s, 1H), 4.58 (d, $J$ = 5.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.8, 138.2, 134.3, 131.6, 128.71, 128.55, 127.82, 127.51, 127.05, 44.0.

**N-Cyclohexylbenzamide** (Table 1, entry 2): Following the general procedure and purification by column chromatography N-cyclohexylbenzamide was obtained as a white solid (0.0824 g, 99% yield); mp 143-144 °C; $R_f$ 0.48 (30% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77-7.75 (m, 2H), 7.49-7.38 (m, 3H), 6.20 (br, s, 1H), 4.02-3.92 (m, 1H), 2.03-2.00 (m, 2H), 1.77-1.72 (m, 2H),
1.67-1.62 (m, 1H), 1.46-1.35 (m, 2H), 1.29-1.16 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.7, 135.1, 131.2, 128.5, 126.9, 48.7, 33.2, 25.56, 24.95.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73-7.40 (m, 5H), 6.03 (br s, 1H), 1.48 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.9, 135.9, 131.0, 128.4, 126.7, 51.6, 28.9.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.35 (m, 5H), 3.56 (br, s, 2H), 3.26 (br, s, 2H), 1.26 (br, s, 3H), 1.10 (br, s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.3, 137.2, 129.1, 128.4, 126.2, 43.3, 39.3, 14.2, 12.9.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (s, 5H), 3.71 (br s, 2H), 3.34 (br s, 2H), 1.67 (br s, 4H), 1.51 (br, s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.3, 136.5, 129.4, 128.4, 126.8, 48.8, 43.1, 26.5, 25.6, 24.6.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J= 7.6$ Hz, 2H), 7.64 (d, $J= 7.6$ Hz, 2H), 7.55-7.44 (m, 3H), 7.36 (t, $J= 7.6$ Hz, 2H), 7.15 (t, $J= 7.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.5, 137.9, 135.0, 131.8, 129.1, 128.7, 127.1, 124.6,120.4.
**N-p-Tolyllbenzamide** (Table 1, entry 7): Following the general procedure and purification by column chromatography, N-p-tolylbenzamide was obtained as a white solid (0.0744 g, 86% yield); mp 158-159 °C; \( R_f \) 0.34 (40% EtOAc/hexanes); \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.79 (d, \( J = 7.2 \) Hz, 2H), 7.47-7.35 (m, 5H), 7.07 (d, \( J = 8.4 \) Hz, 2H), 2.25 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 166.9, 135.4, 134.9, 134.2, 131.6, 129.4, 128.5, 127.2, 120.7, 20.8.

**N-(4-nitrophenyl)benzamide** (Table 1, entry 8): Following the general procedure and purification by column chromatography. N-(4-Nitrophenyl)benzamide was obtained as a yellow solid (0.0269 g, 27% yield); mp 197-198 °C; \( R_f \) 0.40 (20% EtOAc/hexanes); \(^1\)H NMR (400 MHz, CDCl₃+ CD₃OD 3 drops): \( \delta \) 7.85 (d, \( J = 8.4 \) Hz, 2H), 7.26 (br s, 3H), 7.11 (br s, 2H), 6.56 (d, \( J = 8.4 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 160.1, 158.7, 141.3, 133.4, 129.0, 128.42, 128.35, 124.3, 123.0.

**N-cyclohexyl-4-methoxybenzamide** (Table 1, entry 9): Following the general procedure and purification by column chromatography, N-cyclohexyl-4-methoxybenzamide was obtained as a white solid (0.0909 g, 95% yield); mp 159-160 °C; \( R_f \) 0.42 (40% EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.72 (d, \( J = 8.8 \) Hz, 2H), 6.90 (d, \( J = 8.8 \) Hz, 2H), 5.99 (d, \( J = 7.2 \) Hz, 1H), 4.02 (m, 1H), 3.84 (s, 3H), 2.04-2.00 (m, 2H), 1.76-1.72 (m, 2H), 1.66-1.62 (m, 1H), 1.47-1.36 (m, 2H), 1.27-1.18 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 166.2, 162.0, 128.6, 127.4, 133.7, 55.4, 48.6, 33.3, 25.6, 25.0.

**4-Chloro-N-cyclohexylbenzamide** (Table 1, entry 10): Following the general procedure and purification by column chromatography, 4-chloro-N-cyclohexylbenzamide was obtained as a white solid (0.0935 g, 96% yield); mp 186-187 °C; \( R_f \) 0.48 (30% EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.69 (d, \( J = 8.80 \) Hz), 7.36 (d, \( J = 8.80 \) Hz, 2H), 6.22 (s, 1H), 3.98-3.89 (m, 1H), 2.02-1.98 (m, 2H), 1.77-1.72 (m, 2H), 1.68-1.63 (m, 1H), 1.45-1.34 (m, 2H), 1.28-1.12 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 165.6, 137.4, 133.4, 128.7, 128.4, 48.9, 33.1, 25.5, 25.0.
**N-Cyclohexyl-3,5-dinitrobenzamide** (Table 1, entry 11): Following the general procedure and purification by column chromatography, N-cyclohexyl-3,5-dinitrobenzamide was obtained as a white solid (0.1058 g, 88% yield); mp 212-213 °C; $R_f$ 0.48 (30% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 3 drops): $\delta$ 9.03 (t, $J$ = 2.0 Hz, 1H), 8.96 (d, $J$ = 2.0 Hz, 2H), 7.94 (d, $J$ = 7.2 Hz, 1H), 3.91-3.83 (m, 1H), 1.94-1.91 (m, 2H), 1.74-1.71 (m, 2H), 1.63-1.59 (m, 1H), 1.38-1.06 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 3 drops): $\delta$ 162.5, 148.4, 138.5, 127.6, 120.6, 49.9, 32.6, 25.3, 25.0.

**N-Cyclohexylcinnamamide** (Table 1, entry 12): Following the general procedure and purification by column chromatography, N-cyclohexylcinnamamide was obtained as a white solid (0.0817 g, 87% yield); mp 178-179 °C; $R_f$ 0.33 (30% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 (d, $J$ = 15.6 Hz), 7.49-7.47 (m, 2H), 7.33-7.32 (m, 3H), 6.43 (d, $J$ = 15.6 Hz, 1H), 5.88 (s, 1H), 3.96-3.87 (m, 1H), 2.01-1.93 (m, 2H), 1.75-1.70 (m, 2H), 1.64-1.61 (m, 1H), 1.44-1.34 (m, 2H), 1.25-1.12 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.0, 140.6, 135.0, 129.5, 128.8, 127.7, 121.3, 48.4, 33.2, 25.6, 24.9.

**N-Cyclohexyl-5-phenylpentanamide** (Table 1, entry 13): Following the general procedure and purification by column chromatography, N-cyclohexyl-5-phenylpentanamide was obtained as a white solid (0.0797 g, 75% yield); mp 75-76 °C; $R_f$ 0.42 (40% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30-7.27 (m, 2H), 7.21-7.17 (m, 3H), 5.57 (br, s, 1H), 3.81-3.72 (m, 1H), 2.64 (t, $J$ = 6.8 Hz, 2H), 2.17 (t, $J$ = 6.8 Hz, 2H), 1.92-1.88 (m, 2H), 1.73-1.65 (m, 7H), 1.41-1.30 (m, 2H), 1.21-1.06 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.0, 142.3, 128.4, 128.3, 125.8, 48.1, 36.8, 35.7, 33.2, 31.1, 25.6, 24.9.
**N-Benzylnicotinamide** (Table 1, entry 14): Following the general procedure and purification by column chromatography, N-benzylnicotinamide was obtained as a colorless liquid (0.0852 g, 98% yield); \( R_f \) 0.39 (70% EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.93 (s, 3H), 8.60 (dd, \( J = 4.6, 2.0 \) Hz, 1H), 8.13-8.10 (m, 1H), 7.33 (m, 6H), 7.15 (br, s, 1H), 4.60 (dd, \( J = 5.6, 1.6 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 165.6, 152.1, 147.9, 137.8, 135.4, 132.1, 128.8, 127.9, 127.7, 123.5, 44.2.

**3,4-Dimethoxy-N-(pyridin-4-yl)benzamide** (Table 1, entry 15): Following the general procedure and purification by column chromatography, 3,4-dimethoxy-N-(pyridin-4-yl)benzamide was obtained as a white crystal (0.0921 g, 87% yield); mp 85-86 °C; \( R_f \) 0.41 (20% methanol/ethyl acetate); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.75 (s, 1H), 8.46 (d, \( J = 6.0 \) Hz, 2H), 7.62 (d, \( J = 6.0 \) Hz, 2H), 7.46 (d, \( J = 2.0 \) Hz, 1H) 7.44 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 6.84 (d, \( J = 8.4 \) Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 165.9, 152.6, 150.5, 149.3, 145.6, 126.5, 120.1, 114.0, 110.8, 110.3, 56.09, 56.07.

**3,5-Dinitro-N-o-tolylbenzamide** (Table 1, entry 16): Following the general procedure and purification by column chromatography, 3,5-Dinitro-N-o-tolylbenzamide was obtained as a yellow solid (0.1160 g, 94% yield); mp 246-247 °C; \( R_f \) 0.39 (20% EtOAc/hexanes); \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO): \( \delta \) 10.64 (s, 1H), 9.22 (s, 2H), 9.06 (s, 1H), 7.40-7.27 (m, 4H), 2.30 (s, 3H); \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO): \( \delta \) 161.8, 148.7, 137.6, 136.0, 134.4, 131.0, 128.4, 127.2, 126.7, 121.6, 18.3.

**N,N-diethyl-2-naphthamide** (Table 1, entry 17): Following the general procedure and purification by column chromatography, N,N-diethyl-2-naphthamide was obtained as a viscous yellow oil (0.0919 g, 99% yield); \( R_f \) 0.34 (20% EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.88-7.83 (m, 4H), 7.53 (m, 3H), 3.59 (br, s, 2H), 3.29 (br, s, 2H), 1.28 (br, s, 3H), 1.12 (br, s, 3H); \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO): \( \delta \) 159.8, 148.4, 135.6, 134.4, 131.0, 128.5, 127.2, 126.7, 121.6, 18.3.
MHz, CDCl$_3$): δ 171.3, 134.6, 133.4, 132.8, 128.31, 128.19, 127.8, 126.79, 126.61, 125.8, 123.9, 43.4, 39.3, 14.3, 13.0.

Synthesis of amides 3a-i using polymer supported PPh$_3$ (PS-PPh$_3$)

To a stirred solution of iodine (0.62 mmol) in CH$_2$Cl$_2$ (4 mL) was added with one portion of PS–PPh$_3$ (0.62 mmol) at 0 °C. An amine (0.49 mmol) was added with continuously stirred until the amine could not be detected by TLC (within 10-30 min). Subsequently, this mixture was treated with a carboxylic acid (0.41 mmol) and stirred for 5 min, followed by addition of triethylamine (0.82 mmol). The reaction was allowed to warm up to room temperature and stirred until no starting material remained. After that, the mixture was filtered and washed several times with CH$_2$Cl$_2$ and MeOH. The combined filtrate was evaporated to dryness and purified by passing through a short silica gel plug (EtOAc/hexane).

N-Benzyl-4-hydroxybenzamide (Figure 1, 3a): Following the general procedure and purification by column chromatography, N-benzyl-4-hydroxybenzamide was obtained as a white crystal (0.0783 g, 84% yield); mp 135-136 °C; $R_f$ 0.43 (50% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 3 drops): δ 7.60 (d, $J = 8.8$ Hz, 2H), 7.30-7.20 (m, 5H), 7.01 (br, s, 1H), 6.77 (d, $J = 8.8$ Hz, 2H), 4.53 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 3 drops): δ 168.0, 160.3, 138.3, 128.9, 128.6, 127.7, 127.4, 125.1, 115.3, 43.8.

4-Hydroxy-N-phenylbenzamide (Figure 1, 3b): Following the general procedure and purification by column chromatography, 4-hydroxy-N-phenylbenzamide was obtained as a yellow solid (0.0717 g, 82% yield); mp 185-186 °C; $R_f$ 0.36 (40% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 5 drops): δ 7.76 (d, $J = 8.8$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H) 7.32 (t, $J = 8.4$ Hz, 2H), 7.10 (t, $J = 8.4$ Hz, 1H), 6.85 ($J = 8.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 5 drops): δ 167.1, 160.6, 138.4, 129.5, 128.9, 125.9, 124.5, 121.0, 115.4.
N-Benzyl-4-hydroxy-3-methoxybenzamide (Figure 1, 3c): Following the general procedure and purification by column chromatography, N-benzyl-4-hydroxy-3-methoxybenzamide was obtained as a white crystal (0.104 g, 99% yield); mp 169-170 °C; Rf 0.40 (50% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 2 drops): $\delta$ 7.46 (br, s, 1H), 7.39 ($d$, $J$ = 2.0 Hz, 1H), 7.29-7.23 (m, 5H), 7.20 (dd, $J$ = 8.0, 2.0 Hz, 1H), 6.98 (br, s, 1H), 6.81 (d, $J$ = 8.0 Hz, 1H), 4.54 (s, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 2 drops): $\delta$ 167.6, 149.1, 147.0, 138.3, 128.7, 127.7, 127.4, 126.0, 120.0, 114.3, 110.7, 55.9, 43.9.

4-Hydroxy-3-methoxy-N-phenylbenzamide (Figure 1, 3d): Following the general procedure and purification by column chromatography, 4-hydroxy-3-methoxy-N-phenylbenzamide was obtained as a white solid (0.0608 g, 61% yield); mp 142-143 °C; Rf 0.36 (40% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.32 (s, 1H), 7.60 ($d$, $J$ = 8.0 Hz, 2H), 7.45 ($d$, $J$ = 2.0 Hz, 1H), 7.34-7.30 (m, 3H), 7.10 (t, $J$ = 8.0 Hz, 1H), 6.87 (d, $J$ = 8.4 Hz, 1H) 3.86 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.9, 149.3, 147.0, 138.1, 129.0, 126.7, 124.4, 120.4, 120.2, 114.2, 110.7, 56.0.

N-(Pyridin-2-ylmethyl)nicotinamide (Figure 1, 3e): Following the general procedure and purification by column chromatography, N-(pyridin-2-ylmethyl)nicotinamide was obtained as a viscous yellow oil (0.0491 g, 56% yield); Rf 0.50 (70% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.08 (d, $J$ = 2.4 Hz, 1H), 8.67 (dd, $J$ = 5.2, 1.6 Hz, 1H), 8.52 (dt, $J$ = 4.8, 0.8 Hz, 1H), 8.18 (dt $J$ = 8.0, 1.6 Hz, 1H), 7.98 (br, s, 1H), 7.68 (td, $J$ = 8.0, 1.6 Hz, 1H), 7.37 (ddd, $J$ = 8.0, 4.8, 0.8 Hz, 1H), 7.32 (d, $J$ = 8.0 Hz, 1H), 7.20 (dd, $J$ = 8.0, 1.6 Hz, 1H), 4.74 (d, $J$ = 5.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.5, 155.8, 152.2, 149.0, 148.3, 137.0, 135.2, 130.0, 123.5, 122.6, 122.3, 44.6.
4-Amino-N-benzylbenzamide (Figure 1, 3f): Following the general procedure and purification by column chromatography, 4-amino-N-benzylbenzamide was obtained as a colorless liquid (0.0603 g, 65% yield); 

\[ R_f \ 0.31 \ (70\% \ \text{EtOAc/hexane}) \]

\[ ^1H \ NMR \ (400 \ MHz, \ CDCl_3): \delta \ 7.62 \ (J = 8.8 \ Hz, \ 2H), \ 7.35-7.26 \ (m, \ 5H), \ 6.64 \ (br, \ s, \ 1H), \ 6.60 \ (d, \ J = 8.8 \ Hz, \ 2H), \ 4.58 \ (d, \ J = 5.6 \ Hz, \ 2H), \ 4.05 \ (br, \ s, \ 2H); \ ^{13}C \ NMR \ (100 \ MHz, \ CDCl_3): \delta \ 167.4, 150.0, 138.7, 128.8, 128.7, 127.8, 127.4, 123.6, 114.1, 43.9. \]

(3-Aminophenyl)(morpholino)methanone (Figure 1, 3g): Following the general procedure and purification by column chromatography, (3-aminophenyl)(morpholino)methanone was obtained as a viscous yellow oil (0.0382 g, 45% yield); 

\[ R_f \ 0.22 \ (70\% \ \text{EtOAc/hexane}) \]

\[ ^1H \ NMR \ (400 \ MHz, \ CDCl_3): \delta \ 7.09 \ (td, \ J = 7.0, 1.2 \ Hz, \ 1H), \ 6.66-6.62 \ (m, \ 3H), \ 3.69 \ (br, \ s, \ 4H), \ 3.56 \ (br, \ s, \ 2H), \ 3.39 \ (br, \ s, \ 2H); \ ^{13}C \ NMR \ (100 \ MHz, \ CDCl_3): \delta \ 170.7, 14.0, 136.3, 129.4, 116.5, 116.3, 113.3, 66.9, 48.2, 42.5. \]

tert-Butyl (2-(benzylamino)-2-oxoethyl)carbamate (Figure 1, 3h): Following the general procedure and purification by column chromatography, tert-butyl 2-(benzylamino)-2-oxoethylcarbamate was obtained as a yellow liquid (0.1073 g, 99% yield); 

\[ R_f \ 0.47 \ (70\% \ \text{EtOAc/hexane}) \]

\[ ^1H \ NMR \ (400 \ MHz, \ CDCl_3): \delta \ 7.31-7.26 \ (br, \ m, \ 5H), \ 6.87 \ (br, \ s, \ 1H), \ 5.45 \ (br, \ s, \ 1H), \ 4.42 \ (d, \ J = 3.2 \ Hz, \ 2H), \ 3.80 \ (s, \ 2H), \ 1.42 \ (s, \ 9H); \ ^{13}C \ NMR \ (100 \ MHz, \ CDCl_3): \delta \ 169.6, 138.0, 128.7, 127.6, 127.5, 44.4, 44.3, 28.3. \]

Benzyl (S)-(1-(benzylamino)-1-oxo-3-phenylpropan-2-yl)carbamate (Figure 1, 3i): Following the general procedure and purification by column chromatography, (S)-benzyl 1-(benzylamino)-1-oxo-3-
phenylpropan-2-ylcarbamate was obtained as a white solid (0.0796 g, 50% yield); mp 160-161 °C; $R_f$ 0.47 (40% EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.03 (m, 15H), 6.98 (br, s, 1H), 5.94 (br, d, $J = 8.0$ Hz, 1H), 4.99 (dd, $J = Hz$, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.22, 156.2, 137.5, 136.4, 129.4, 128.61, 128.55, 128.52, 128.18, 127.93, 127.62, 127.38, 126.9, 67.0, 56.3, 43.3, 38.8.
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
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$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 3 drops); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 3 drops)
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$\text{H NMR (400 MHz, CDCl}_3); \; ^{13}\text{C NMR (100 MHz, CDCl}_3)\)$
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 3 drops); 13C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 3 drops)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$\textsuperscript{1}H$ NMR (400 MHz, CDCl$_3$); $\textsuperscript{13}C$ NMR (100 MHz, CDCl$_3$)
\[^1\text{H}\text{ NMR (400 MHz, CDCl}_3\text{)}; \]^13\text{C NMR (100 MHz, CDCl}_3\text{)}\]
$\text{H NMR (400 MHz, CDCl}_3$; $\text{C NMR (100 MHz, CDCl}_3$)
$^1$H NMR (400 MHz, (CD$_3$)$_2$SO); $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO)
\(^1\)H NMR (400 MHz, CDCl\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\))
$^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 3 drops); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 3 drops)
$^1$H NMR (400 MHz, CDCl$_3$+ CD$_3$OD 5 drops); $^{13}$C NMR (100 MHz, CDCl$_3$+ CD$_3$OD 5 drops)
$^1$H NMR (400 MHz, CDCl$_3$ + CD$_3$OD 2 drops); $^{13}$C NMR (100 MHz, CDCl$_3$ + CD$_3$OD 2 drops)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
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$^{1}$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)

- [Chemical structure diagram]

- [NMR spectrum image]

- [NMR spectrum image]
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{H NMR (400 MHz, CDCl}_3\); \text{C NMR (100 MHz, CDCl}_3\)
$^1$H NMR (400 MHz, CDCl$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$)
Figure S1. $^{31}$P{H}-NMR monitoring the progress of the reaction between benzoic acid and benzylamine in CDCl$_3$ following the method A: (a) Ph$_3$P, (b) the solution after addition of I$_2$, (c) the reaction after adding benzoic acid, (d) the reaction after addition of Et$_3$N, and (e) the reaction after addition of benzylamine.

Figure S2. $^{31}$P{H}-NMR monitoring the progress of the reaction between benzoic acid and benzylamine in CDCl$_3$ following the method B: (a) Ph$_3$P, (b) the solution after addition of I$_2$, (c) the reaction after adding benzylamine, (d) the reaction after addition of Et$_3$N, and (e) the reaction after addition of benzoic acid.
**Figure S3.** $^{31}$P{H}-NMR monitoring the progress of the reaction between benzoic acid and benzylamine in CDCl$_3$ following the method C; (a) Ph$_3$P, (b) the solution after addition of I$_2$, (c) the reaction after adding benzoic acid, (d) the reaction after addition of benzylamine, and (e) the reaction after addition of Et$_3$N.

**Figure S4.** $^{31}$P{H}-NMR monitoring the progress of the reaction between benzoic acid and benzylamine in CDCl$_3$ following the method D; (a) PPh$_3$, (b) the solution after addition of I$_2$, (c) the reaction after adding benzylamine, (d) the reaction after addition of benzoic acid, and (e) the reaction after addition of Et$_3$N.
Figure S5  ESI-MS spectrum of the crude reaction between benzylamine and benzoic acid after adding Et$_3$N.