Combined Experimental and Computational Study of Al$_2$O$_3$ Catalyzed Transamidation of Secondary Amides with Amines.
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1. Synthesis of N-Phenyl Benzamide

For synthesis of N-Phenyl Benzamide, N- Methyl Benzamide (1 mmol) and aniline (1 mmol) were taken in a RB flask containing 5 mol% Al₂O₃ and then added 5 mL Triethyl amine in the mixture. This reaction mixture was heated on hot plate around at 100 °C for 30 h in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction was monitored by TLC with n-hexane and chloroform. Completion of the reaction was confirmed by TLC. After the completion of the reaction, 4 ml 2-propanol was added to dissolve amides mixture. Then, Al₂O₃ was separated from the mixture by centrifugation followed by washing with acetone and dried at 100°C for 3 h. The recovered Al₂O₃ was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique with ethanol and water. For catalyst screening, solvent screening and temperature screening same reaction procedure were performed.

![Scheme S1: Synthesis of N-Phenyl Benzamide.](image)

- Molecular weight : 197 g/mol
- Molecular formula : C₁₃NOH₁₁
- Solubility : Soluble in Chloroform.
- FT-IR (υ KBr) : 3347, 3055, 1659, 1536, 1439, 1659, 1075 cm⁻¹
- 1H-NMR (400 MHz, CDCl₃) : δ 8.02 (br s, 1H, -NH), 7.088(m, 2H), 7.67 (m, 2H), 7.48 (t, 1H), 7.38 (t, 2H), 7.27(m, 2H), 7.17 (t, 1H)
- 13C-NMR (100 MHz, CDCl₃) : δ 165.895 (1C, C=O), 137.969 (1C), 135.010 (1C), 131.844 (1C), 129.100-129.438 (2C), 128.783-129.074 (2C), 127.080 (2C), 124.550 (1C), 120.30 (2C)
2. Synthesis of N-(o-methyl) Phenyl Benzamide

For synthesis of N-(o-methyl) Phenyl Benzamide, N- Methyl Benzamide (1 mmol) and o-Toluedine (1 mmol) were taken in a RB flask containing 5 mol% Al₂O₃ and then added 5 mL Triethyl amine in the mixture. This reaction mixture was heated on hot plate around at 100 °C for 30 hrs in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction was monitored by TLC with n-hexane and chloroform. Completion of the reaction was confirmed by TLC. After the completion of the reaction, 4 ml 2-propanol was added to dissolve amides mixture. Then, Al₂O₃ was separated from the mixture by centrifugation followed by washing with acetone and dried at 100°C for 3 hrs. The recovered Al₂O₃ was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique with ethanol and water. For catalyst screening, solvent screening and temperature screening same reaction procedure were performed.

![Scheme S2: Synthesis of N-(o-methyl) Phenyl Benzamide.]

- Molecular weight : 212 g/mol
- Molecular formula : C₁₄NOH₁₄
- Solubility : Soluble in Chloroform.
- FT-IR (υ KBr) : 3227, 3060, 1645, 1592, 1434, 1294, 1074cm⁻¹
- 1H-NMR (400 MHz, CDCl₃) : δ 8.067 (br s, 1H, -NH), 7.86-7.88 (m, 2H), 7.53-7.56 (t, 2H), 7.44-7.47 (t, 3H), 7.23-7.28 (m, 2H), 6.69-6.99 (m, 1H), 2.36 (s, 3H)
- 13C-NMR (100 MHz, CDCl₃) : δ 165.924 (1C, C=O), 138.989 (1C), 137.913 (1C), 131.764 (1C), 129.391 (1C), 128.86 (1C), 128.729 (2C), 125.401 (1C), 127.092 (2C), 121.031 (1C), 117.462 (1C), 21.51 (1C).
3. Synthesis of N-n-Octyl Benzamide

For synthesis of N-n-Octyl Benzamide, N- Methyl Benzamide (1 mmol) and n-Octyl amine (1 mmol) were taken in a RB flask containing 5 mol% Al$_2$O$_3$ and then added 5 mL Triethyl amine in the mixture. This reaction mixture was heated on hot plate around at 100 °C for 30 hrs in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction was monitored by TLC with n-hexane and chloroform. Completion of the reaction was confirmed by TLC. After the completion of the reaction, 4 ml 2-propanol was added to dissolve amides mixture. Then, Al$_2$O$_3$ was separated from the mixture by centrifugation followed by washing with acetone and dried at 100°C for 3 hrs. The recovered Al$_2$O$_3$ was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique with ethanol and water. For catalyst screening, solvent screening and temperature screening same reaction procedure were performed.

![Scheme S3: Synthesis of N-Octyl Benzamide.](image)

- Molecular weight : 233 g/mol
- Molecular formula : C$_{15}$NOH$_2$$_3$
- Solubility : Soluble in Chloroform.
- FT-IR (υ KBr) : 3360, 3058, 1653, 1549, 1493, 1447, 1076cm$^{-1}$
- 1H-NMR (400 MHz, CDCl3) : δ 6.368 (br s, 1H, -NH), 7.77-7.78 (m, 2H), 7.47-7.51 (t, 1H), 7.40-7.44 (t, 2H), 3.42-3.47 (m, 2H), 2.362-2.398 (m, 2H), 1.58-1.65 (m, 2H), 1.28-1.34 (m, 8H), 0.87-.91 (t, 3H)
- 13C-NMR (100 MHz, CDCl3) : δ 167.626 (1C, C=O), 134.811 (1C), 131.313 (1C), 128.525 (1C), 126.889 (1C), 40.181 (1C), 31.806 (1C), 29.675 (1C), 29.225 (1C), 29.308 (1C), 27.029 (1C), 14.097 (1C).
4. Synthesis of N-(m-methyl) Phenyl Benzamide

For synthesis of N-(m-methyl)Phenyl Benzamide, N- Methyl Benzamide (1 mmol) and m-Toluedine (1 mmol) were taken in a RB flask containing 5 mol% Al$_2$O$_3$ and then added 5 mL Triethyl amine in the mixture. This reaction mixture was heated on hot plate around at 100 °C for 30 hrs in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction was monitored by TLC with n-hexane and chloroform. Completion of the reaction was confirmed by TLC. After the completion of the reaction, 4 ml 2-propanol was added to dissolve amides mixture. Then, Al$_2$O$_3$ was separated from the mixture by centrifugation followed by washing with acetone and dried at 100°C for 3 hrs. The recovered Al$_2$O$_3$ was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique with ethanol and water. For catalyst screening, solvent screening and temperature screening same reaction procedure were performed.

Scheme S4: Synthesis of N-(o-methyl)Phenyl Benzamide.

- Molecular weight : 212 g/mol
- Molecular formula : C$_{14}$NOH$_{14}$
- Solubility : Soluble in Chloroform.
- FT-IR (υ KBr) : 3240, 3030, 2829, 1651, 1603, 1526, 1440cm$^{-1}$
- 1H-NMR (400 MHz, CDCl3) : δ 7.722 (br s, 1H, -NH), 7.962-7.982 (m, 1H), 7.907-7.925 (m, 1H), 7.576-7.612 (t, 1H), 7.50-7.54 (m, 3H), 7.24-7.27 (m, 1H), 7.13 (m, 1H), 2.36 (s, 3H)
- 13C-NMR (100 MHz, CDCl3) : δ 165.683 (1C, C=O), 135.789 (1C), 135.039 (1C), 131.885 (1C), 130.591 (1C), 129.244 (1C), 128.873-128.918 (2C), 127.074 (1C), 126.947 (1C), 125.399 (1C), 123.139 (1C), 17.860 (1C).
5. Synthesis of N-Benzyl Benzamide

For synthesis of N-Benzyl Benzamide, N- Methyl Benzamide (1 mmol) and Benzylamine (1 mmol) were taken in a RB flask containing 5 mol% Al₂O₃ and then added 5 mL Triethyl amine in the mixture. This reaction mixture was heated on hot plate around at 100 °C for 30 hrs in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction was monitored by TLC with n-hexane and chloroform. Completion of the reaction was confirmed by TLC. After the completion of the reaction, 4 ml 2-propanol was added to dissolve amides mixture. Then, Al₂O₃ was separated from the mixture by centrifugation followed by washing with acetone and dried at 100°C for 3 hrs. The recovered Al₂O₃ was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique with ethanol and water. For catalyst screening, solvent screening and temperature screening same reaction procedure were performed.

Scheme S5: Synthesis of N-Benzyl Benzamide.

- Molecular weight : 212 g/mol
- Molecular formula : C₁₄NOH₁₃
- Solubility : Soluble in Chloroform.
- FT-IR (υ KBr) : 3329, 3056, 2940, 1639, 1578, 1555, 1492 cm⁻¹
- ¹H-NMR (400 MHz, CDCl₃) : δ 9.270 (br s, 1H, -NH), 5.150 (s, 1H), 4.460 (s, 1H), 6.825-6.834 (m, 2H), 7.396-7.404 (m, 2H), 7.185-7.283 (m, 1H), 8.001-8.183 (m, 2H), 7.597-7.641 (m, 2H), 7.826-7.844 (m, 1H)
6. Catalyst Screening

Model reaction:

\[
\begin{align*}
\text{Catalyst Screenin} & \text{g for model reaction} \\
\text{Table S1: Catalyst screening for model reaction} \\
\begin{array}{|c|c|c|}
\hline
\text{Entry} & \text{Catalyst} & \text{% of Yields} \\
\hline
01 & - & 0 \\
02 & \text{SnO}_2 & 5 \\
03 & \text{Cu}_2\text{O} & 3 \\
04 & \text{Al}_2\text{O}_3 & 76 \\
05 & \text{Nb}_2\text{O}_5 & 8 \\
06 & \text{CeO}_2 & 10 \\
07 & \text{TiO}_2 & 6 \\
\hline
\end{array}
\end{align*}
\]

Figure S1: Catalyst screening for model reaction.
7. Solvent Screening

Model reaction.

![Chemical reaction diagram]

Table S2: Solvent screening for model reaction

| Entry | Solvent       | % of Yields |
|-------|---------------|-------------|
| 01    | No solvent    | 0           |
| 02    | O-Xylene      | 9           |
| 03    | Benzene       | 5           |
| 04    | Triethylamine | 76          |
| 05    | Toluene       | 7           |

Figure S2: Solvent screening for model reaction.
8. Reusability of Al$_2$O$_3$

Model Reaction:

$$\begin{align*}
\text{NH}_{\text{CH}_3} & + \text{H}_3\text{C}\begin{array}{c}
\text{NH}_2
\end{array} \\
\xrightarrow{\text{Al}_2\text{O}_3, \ 5 \ \text{mol} \ % \ \text{Solvent \ Reflux}} & \xrightarrow{\text{Al}_2\text{O}_3} \\
\text{O} & + \text{H}_2\text{N}_\text{CH}_3
\end{align*}$$

Table S3: Reusability of Al$_2$O$_3$ for model reaction.

| Cycle Number | Catalyst | % of Yields |
|--------------|----------|-------------|
| 01           |          | 76          |
| 02           | Al$_2$O$_3$ | 70          |
| 03           |          | 63          |
| 04           |          | 41          |

Figure S3: Reusability of Al$_2$O$_3$ for model reaction.
9. Optimize structure of Compounds 1-5

Table S4: Optimize Structure of Compounds 1-5

| Compnd | Optimize ball and bond type Structure | Optimize tube Structure | Optimize Energy (Hartee) |
|--------|---------------------------------------|-------------------------|--------------------------|
| 1      | ![Image](image1.png)                  | ![Image](image2.png)    | -624.166                 |
| 2      | ![Image](image3.png)                  | ![Image](image4.png)    | -663.353                 |
| 3      | ![Image](image5.png)                  | ![Image](image6.png)    | -706.818                 |
| 4      | ![Image](image7.png)                  | ![Image](image8.png)    | -663.355                 |
| 5      | ![Image](image9.png)                  | ![Image](image10.png)   | -663.351                 |
10. DFT Calculation Data

Table S5: Using Catalyst Al$_2$O$_3$

| Calculation Method | Basis Set          | Compounds     | Energy (Hartee) | Relative Energy |
|--------------------|--------------------|---------------|-----------------|-----------------|
| RB3LYP             | 6-311+G (D, P)     | Amides        | -440.380        | 0.000           |
| RB3LYP             | 6-311+G (D, P)     | Amines-1      | -287.631        | 152.749         |
| RB3LYP             | 6-311+G (D, P)     | Catalyst Al$_2$O$_3$ | -710.733     | -270.353        |
| RB3LYP             | 6-311+G (D, P)     | Solvent N(C$_2$H$_5$)$_3$ | -174.528   | 265.853         |
| RB3LYP             | 6-311+G (D, P)     | TS1           | -1438.224       | -997.844        |
| RB3LYP             | 6-311+G (D, P)     | TS2           | -1603.740       | -1163.359       |
| RB3LYP             | 6-311+G (D, P)     | Product 1     | -624.166        | -191.786        |

Table S6: Using Catalyst Nb$_2$O$_5$

| Calculation Method | Basis Set          | Compounds     | Energy (Hartee) | Relative Energy |
|--------------------|--------------------|---------------|-----------------|-----------------|
| RB3LYP             | 6-311+G (D, P)     | Amides        | -440.380        | 0.000           |
| RB3LYP             | 6-311+G (D, P)     | Amines-1      | -287.631        | 152.749         |
| RB3LYP             | 6-311+G (D, P)     | Catalyst Nb$_2$O$_5$ | -7843.992       | -7403.612       |
| RB3LYP             | 6-311+G (D, P)     | Solvent N(C$_2$H$_5$)$_3$ | -174.528       | 265.853         |
| RB3LYP             | 6-311+G (D, P)     | TS1           | -0.430672       | 439.950         |
| RB3LYP             | 6-311+G (D, P)     | TS2           | -8852.090       | -8411.710       |
| RB3LYP             | 6-311+G (D, P)     | Product 1     | -624.166        | -191.786        |

Total energy plot for compounds 1-5

![Total Energy Plot for Compounds 1 and 2](image)
11. Spectra of compound 1

Figure S4: FT-IR spectrum of Compound 1
Figure S5: $^1$H-NMR spectrum of compound 1
Figure S6: Extended $^1$H-NMR spectrum of compound 1.
Figure S7: $^{13}$C-NMR spectrum of compound 1.
Figure S8: Extended $^{13}$C-NMR spectrum of compound 1.
Figure S9: GC-MS spectrum of compound 1.
Figure S10: FT-IR spectrum of compound 2
Figure S11: $^1$H-NMR spectrum of compound 2
Figure S12: Extended $^1$H-NMR spectrum of compound 2
Figure S13: $^{13}$C-NMR spectrum of compound 2.
Figure S14: Extended $^{13}$C-NMR spectrum of compound 2.
Figure S15: GC-MS spectrum of compound 2.
Figure S16: FT-IR spectrum of compound 3.
Figure S17: $^1$H-NMR spectrum of compound 3
Figure S18: Extended $^1$H-NMR spectrum of compound 3
Figure S19: Extended $^1$H-NMR spectrum of compound 3.
Figure S20: $^{13}$C-NMR spectrum of compound 3
Figure S21: Extended $^{13}$C-NMR spectrum of compound 3
Figure S22: GC-MS spectrum of compound 3
14. Spectra of compound 4

Figure S23: FT-IR spectrum of compound 4.
Figure S24: $^1$H-NMR spectrum of compound 4
Figure S25: Extended $^1$H-NMR spectrum of compound 4
Figure S26: $^{13}$C-NMR spectrum of compound 4
Figure S27: Extended $^{13}\text{C}$-NMR spectrum of compound 4
Figure S28: GC-MS spectrum of compound 4
15. Spectra of compound 5

![Figure S29: FT-IT spectrum of compound 5](image_url)
