# Chapter 3

# Cerium Catalyzed Transamidation of Secondary Amides under Ultrasound Irradiation: A Breakthrough in Organic Synthesis

## 3.1 Introduction

Interconversion of one functional group with other is an important strategy used in chemical transformation (Corey et al. 1996, Carey et al. 2002, Hudlicky et al. 2007). Nucleophilic substitution of less nucleophilic leaving group with more nucleophilic group is a simple technique and allow easy synthetic route and a plethora of methods are available in the literature for these interconversions but interconversion between same functional group like transesterification (Meher et al. 2006, Hatta 2010), transamidation (Meister 2009, Lanigan et al. 2013) does not proceed easily due to thermoneutral exchange and is always a challenging task for research fraternity. Transamidation is the process of conversion of one amide group with another amide. Carboxamide group is very important and integral part of many biological (Eisenberg 2003) and industrial polymers (Marchildon 2011), bioactive natural products (Tan 2007), pharmaceuticals (Lichtman et al. 2002, e Sana et al. 2011, Anisimova et al. 2013, Spasov et al. 2013, Tang et al. 2013, Antoszczak et al. 2014) and agrochemicals (Smith et al. 2005, Tsikolia et al. 2013) and also plays an important role in the prevention as well as treatment of various diseases. **Figure 3.1** shows some medicinally important compounds containing carboxamide group like Mozavaptan (**A**) is a hyponatremia drugs, Penicillin (**B**) is an anti-bacterial drug,

Ilepcimide (**C**) is an anticonvulsant drug, Acebutolol (**D**) is a cardiselective beta blocker and Niaprazine (**E**) is a sedative hyponotic drug.

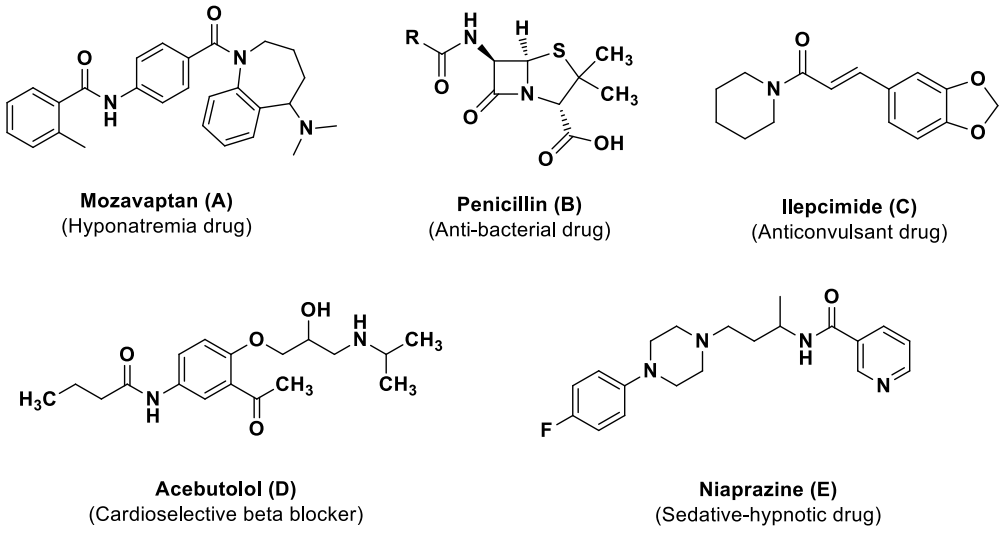


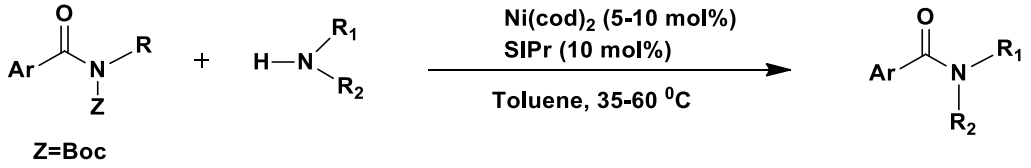

**Figure 3.1:** Some medicinally important molecules containing the amide group.

Although primary amide transamidation was achieved by using various catalysts (Starkov et al. 2011, Atkinson et al. 2012, Arefi et al. 2016, Durgaiah et al. 2016, Rao et al. 2016, Sheng et al. 2017) while the secondary amide transamidation is not much explored till date. Over the past decades only few methodologies have been described for secondary amide transamidation. Bertrand et al. reported for the first time in 1994, the use of excess $AlCl_3$ to promote the transamidation of simple substrates (Bon et al. 1994). Stahl et al. utilized a dimeric aluminum complex, $Al_2(NMe_2)_6$, for secondary amide transamidation and due to thermodynamic stability, equilibrium mixture of both the substrate and product were obtained (Eldred et al. 2003). In both the cases the transamidation was carried out by Lewis

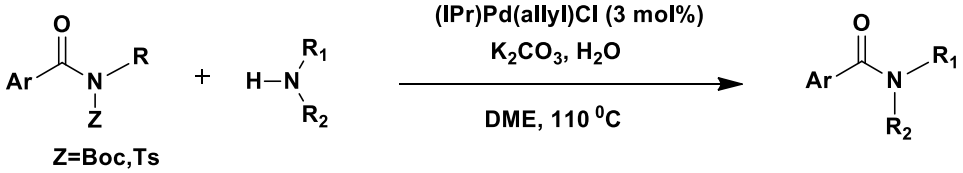
acid activation of the amide carbonyl. Recently, Garg et al. reported secondary amide transamidation by using Ni catalyst in toluene (Baker et al. 2016, Dander et al. 2017) and Szostak reported two simple protocols by using Pd[NHC] complexes (Meng et al. 2017, Shi et al. 2017) and Lewis base catalyst (Liu et al. 2017, Liu et al. 2018) (**Scheme 3.1**). The major limitations of some of these existing protocols are the use of excess of catalysts, sensitive and expensive ligands or high reaction temperature or longer reaction time. Despites of these discoveries, the development of a simple and efficient method to achieve secondary amide transamidation under mild condition is desirable and of great interest.

The challenge in transamidation of secondary amides under mild condition is twofold (1) high energy barrier to nucleophilic addition due to resonance stabilization (Pauling et al. 1951, Greenberg et al. 2000), (2) unfavorable thermodynamics of the transamidation process (Mucsi et al. 2008). In view of the above challenges noted earlier we describe here a facile and efficient protocol to accomplish the transamidation of secondary amides. The two main challenges for this process have been workout as follows (a) the kinetic energy barrier for the system have been reduced by activating nitrogen of the amide group with electron withdrawing trifluoroacetyl group because it makes amide bond twisted which decrease the resonance and weaken the C-N bond (Pace et al. 2016, Szostak et al. 2016, Meng et al. 2018) and (b) the thermodynamic challenge of thermoneutral exchange is resolved as removal of less nucleophilic amine by more nucleophilic amine and using cerium catalyst to facilitate C–N bond cleavage (**Scheme 3.2**).

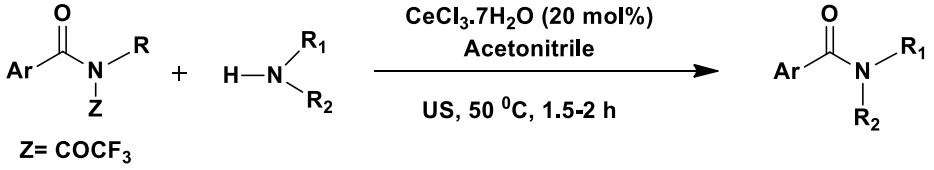
**A:** Ni catalyzed secondary carboxamides transamidation via C–N bond cleavage




**B:** Pd catalyzed transamidation of carboxamides via C–N bond cleavage




**C: Present work;** Ce catalyzed transamidation of secondary carboxamides via C–N bond cleavage under ultrasound irradiation



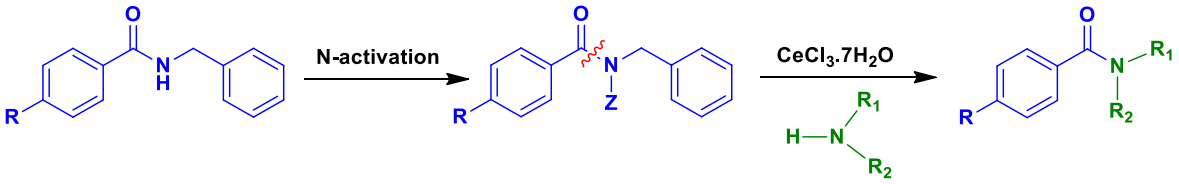

**Scheme 3.1:** Ni and Pd metal catalyzed transamidation reaction of secondary amides with amines: (**A-B**) Previous work and (**C**) **Present work**; Ce catalyzed transamidation of secondary amides.

Nowadays, lanthanide reagents are widely used in organic transformations, since out of all the lanthanide cerium is most abundant element even more than transition metals like cobalt and zinc. Cerium (III) is most stable oxidation state of cerium and $CeCl_3.7H_2O$

is most common source to obtain this, both hydrated as well as anhydrous form of cerium chloride were used in organic synthesis. The selection of cerium as catalyst in this reaction is based due to its high stability, nontoxicity, acidic nature, high catalytic efficiency, easy isolation, reusability, water tolerant and operational simplicity (Imamoto et al. 1989, Montalban et al. 1999, Kidwai et al. 2010, Jia et al. 2005).

Over the past few decades, many non-conventional energy sources such as microwave irradiation, ultrasound irradiation and photo activated process become very popular in synthetic organic transformations. Among these non-conventional energy sources ultrasound irradiations is one of the powerful method and widely used in organic reactions as well as for nanoparticle synthesis. Ultrasonication offers several advantages like high yield, substantial decrease in reaction time, high selectivity, mild reaction conditions and operational simplicity. Simultaneously ultrasound irradiation lowers the energy consumption, minimum pollution, minimum solvent use and minimum side reaction etc. makes the ultrasound irradiation a greener technique (Banerjee 2017, Banerjee 2017, Banerjee 2017).

In order to improve the yield, rate of reaction, selectivity and operational simplicity ultrasound irradiation technique have been used. Herein, we describe the first cerium catalyzed transamidation of N-$COCF_3$ activated secondary amides under ultrasound irradiation (**Scheme 3.2**).



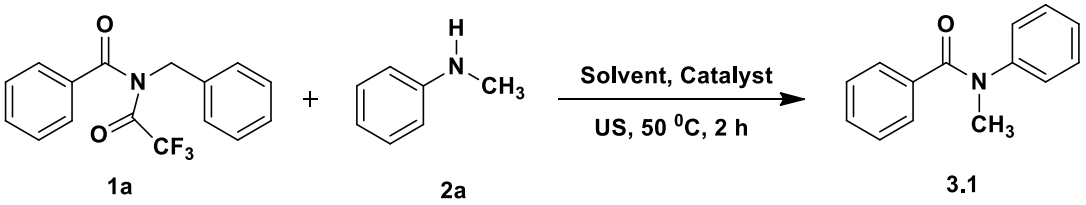

**Scheme 3.2:** Two-step approach for secondary amides transamidation using $CeCl_3.7H_2O$ catalyst.

## 3.2 Results and Discussion

We began our investigations with the reaction of *N*-benzylbenzamide and *N*-methyl aniline (**2a**) and the reaction was performed in acetonitrile under conventional heating method at 80 $^0$C without using any catalyst and as expected no product was obtained even after 24 h. Thereafter, we activated secondary amide *N*-benzylbenzamide with trifluoroacetyl group and its reaction was performed with *N*-methyl aniline (**2a**) under same reaction condition and even after 24 h, no product was obtained. Therefore, we planned for double activation method and selected $CeCl_3.7H_2O$ as a Lewis acid catalyst which supposed to help in weakening the amide C–N bond and promote the transamidation reaction. A reaction was performed between *N*-benzyl-N-(2,2,2-trifluoroacetyl)benzamide (**1a**) and *N*-Methyl aniline (**2a**) using $CeCl_3.7H_2O$ (50 mol%) catalyst in acetonitrile and refluxed for 24 h, 65% yield of transamidated product (**3.1**) was obtained. This result shows that for transamidation, along with N-activation, cerium catalyst is necessary.

To optimize the reaction conditions the reaction between *N*-benzyl-N-(2,2,2-trifluoroacetyl)benzamide (**1a**) and *N*-Methyl aniline (**2a**) was chosen as model reaction. To improve the reaction rate and yield the model reaction was performed in acetonitrile using $CeCl_3.7H_2O$ (50 mol%) catalyst under ultrasonication, a dramatic improvement was observed and in 2 h, 86% yield of desired transamidated product was obtained. For further optimization of reaction conditions, the model reaction was performed under ultrasonication and the results are summarized in **Table 3.1**. The solvent optimization was carried out in various nonpolar and polar solvents like toluene, xylene, 1,2-dichloroethane, water, DMSO, DMF ethanol and THF with 50 mol% of $CeCl_3.7H_2O$ (**Table 3.1, Entries 1-9**) and among all the solvent tested on model reaction acetonitrile was found to be the best solvent. Further the optimum amount of $CeCl_3.7H_2O$ catalyst was investigated and it was observed that 20 mol% catalyst amounts is optimum for the reaction and any further increase in catalyst amount does not improve the reaction rate as well as yield while that of decrease in catalyst amount diminishes the reaction (**Table 3.1, Entries 10-11**). After optimizing the solvent further, we had also tried some other catalysts such as $Ni(NO_3)_6.6H_2O$, $Cu(OAc)_2$, $Zn(OAc)_2$, $CoCl_2$, CuCl, $MnO_2$, $Mn(OAc)_2$, *p*-TSA, $NiCl_2$, $FeCl_3$ and anhydrous $AlCl_3$ (**Table 3.1, Entries 12-22)** but the best yield was obtained in case of $CeCl_3.7H_2O$ (20 mol%).

**Table 3.1:** Effect of different solvents and catalysts on the yield of the product **3.1** under ultrasound irradiation[a]




| Entry | Catalyst (mol%) | Solvent | Yield (%)[b] |
|---|---|---|---|
| 1 | $CeCl_3$. $7H_2O$ (50) | Toluene | <5 |
| 2 | $CeCl_3$. $7H_2O$ (50) | Xylene | 7 |
| 3 | $CeCl_3$. $7H_2O$ (50) | 1,2-Dichloroethane | 15 |
| 4 | $CeCl_3$. $7H_2O$ (50) | Water | 30 |
| 5 | $CeCl_3$. $7H_2O$ (50) | DMSO | 25 |
| 6 | $CeCl_3$. $7H_2O$ (50) | DMF | 20 |
| 7 | $CeCl_3$. $7H_2O$ (50) | Ethanol | 46 |
| 8 | $CeCl_3$. $7H_2O$ (50) | THF | 12 |
| 9 | $CeCl_3$. $7H_2O$ (50) | Acetonitrile | 86 |
| **10** | **$CeCl_3$. $7H_2O$ (20)** | **Acetonitrile** | **86** |
| 11 | $CeCl_3$. $7H_2O$ (10) | Acetonitrile | 73 |
| 12 | $Ni(NO_3)_6.6H_2O$ (20) | Acetonitrile | 45 |
| 13 | $Cu(OAc)_2$ (20) | Acetonitrile | 25 |
| 14 | $Zn(OAc)_2$ (20) | Acetonitrile | 32 |
| 15 | $CoCl_2$ (20) | Acetonitrile | 12 |
| 16 | CuCl (20) | Acetonitrile | 15 |
| 17 | $MnO_2$ (20) | Acetonitrile | 30 |
| 18 | $Mn(OAc)_2$ (20) | Acetonitrile | 35 |
| 19 | *p*-TSA (20) | Acetonitrile | N.R. |
| 20 | $NiCl_2$ (20) | Acetonitrile | 55 |
| 21 | $FeCl_3$ (20) | Acetonitrile | 45 |
| 22 | Anhydrous $AlCl_3$ (20) | Acetonitrile | 60 |

[a] **Reaction condition:** Amide **(1a) (**1.0 mmol) with amine (**2a**) (1.2 mmol) and catalyst in 1mL solvent, under ultrasound irradiation (750 W, 5000 J, 50 $^0$C) for 2 h. [b] Isolated yield.

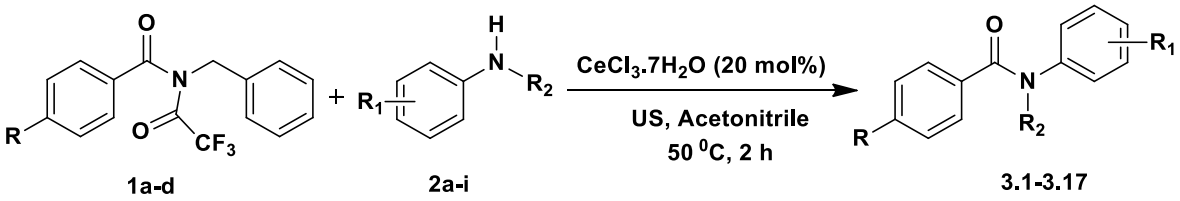
The cerium catalyst was easily recovered and reused upto 5 runs without any significant decrease in catalytic activity and after 5$^{th}$ run 79% yield of the product was obtained. Finally, we had optimized the probe temperature and was found that 50 $^{0}$C is the optimum temperature for the reaction any further increase in probe temperature does not show any improvement on reaction time and yield.

Having optimized reaction conditions in hand (**Table 3.1, Entry 10**), we further investigate the substrate scope for this methodology over a variety of substituted *N*-trifluoroacetyl activated amides *viz.* *N*-benzyl-*N*-(2,2,2-trifluoroacetyl)benzamide (**1a**), *N*-benzyl-4-methoxy-*N*-(2,2,2-trifluoroacetyl)benzamide (**1b**), *N*-benzyl-4-nitro-*N*-(2,2,2-trifluoro acetyl)benzamide (**1c**) and *N*-benzyl-*N*-(2,2,2-trifluoroacetyl)-4-(trifluoromethyl) benzamide (**1d**) with variety of $1^{0}$, $2^{0}$ aliphatic and aromatic amines (**2**) *viz.* *N*-methylaniline (**2a**), *p*-methoxyaniline (**2b**), *p*-nitroaniline (**2c**), aniline (**2d**), *o*-chloroaniline (**2e**), *p*-chloroaniline (**2f**), *o*-methoxyaniline (**2g**), *p*-fluoroaniline (**2h**), *p*-cyanoaniline (**2i**), benzylamine (**2j**), cyclohexylamine (**2k**), cyclopropyl amine (**2l**), methylamine (**2m**), *n*-butylamine (**2n**), dioctylamine (**2o**), pipridine (**2p**), morpholine (**2q**), piprazine (**2r**), 2-ethylaniline (**2s**), 2,6-dimethylaniline (**2t**), adamantylamine (**2u**) and *tert*-butylamine (**2v**) under optimized reaction conditions. On completion of reaction, catalyst was filter off. Acetonitrile was evaporated under reduced pressure and reaction mixture was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to give almost pure product (**3.1**-**3.35**).

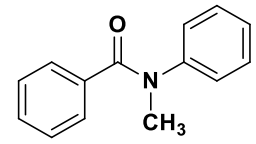
In case if required recrystallization and column chromatography were performed for further purification to obtain pure transamidated product **3** *viz.* *N*-methyl-*N*-phenylbenzamide (**3.1**), 4-methoxy-*N*-methyl-*N*-phenylbenzamide (**3.2**), *N*-methyl-4-nitro-*N*-phenylbenzamide (**3.3**), *N*-methyl-*N*-phenyl-4-(trifluoromethyl)benzamide (**3.4**), *N*-(4-methoxyphenyl) benzamide (**3.5**), 4-methoxy-*N*-(4-methoxy phenyl)benzamide (**3.6**), *N*-(4-methoxyphenyl)-4-nitrobenzamide (**3.7**), *N*-(4-methoxyphenyl)-4-(trifluoromethyl) benzamide (**3.8**), *N*-(4-nitrophenyl)benzamide (**3.9**), 4-methoxy-*N*-(4-nitrophenyl) benzamide (**3.10**), 4-nitro-*N*-(4-nitrophenyl)benzamide (**3.11**), *N*-phenylbenzamide (**3.12**), *N*-(2-chlorophenyl)benzamide (**3.13**), *N*-(4-chlorophenyl) benzamide (**3.14**), *N*-(2-methoxyphenyl)benzamide (**3.15**), *N*-(4-fluorophenyl)benzamide (**3.16**), *N*-(4-cyanophenyl)benzamide (**3.17**), *N*-benzyl benzamide (**3.18**), *N*-benzyl-4-methoxybenzamide (**3.19**), *N*-benzyl-4-(trifluoromethyl) benzamide (**3.20**), *N*-cyclohexyl benzamide (**3.21**), *N*-cyclohexyl-4-methoxybenzamide (**3.22**), *N*-cyclohexyl-4-nitro benzamide (**3.23**), *N*-cyclohexyl-4-(trifluoromethyl)benzamide (**3.24**), *N*-cyclopropyl benzamide (**3.25**), *N*-methylbenzamide (**3.26**), *N*-butylbenzamide (**3.27**), *N*,*N*-dioctyl benzamide (**3.28**), phenyl(piperidin-1-yl)methanone (**3.29**), morpholino(phenyl)methanone (**3.30**), piperazine-1,4-diylbis(phenylmethanone) (**3.31**), *N*-(2-ethylphenyl)benzamide (**3.32**), *N*-(2,6-dimethylphenyl)benzamide (**3.33**), *N*-((3s,5s,7s)-adamantan-1-yl)benzamide (**3.34**) and *N*-(tert-butyl)benzamide (**3.35**). All the tested amines and amides gave the desired products in good to excellent yields (**Scheme 3.3**, **3.4** and **3.5**).

It is observed that aromatic amines with electron donating groups (e.g. methyl and methoxy) showed higher reactivity than the amines having electron withdrawing groups (e.g. –Cl, –Br, $–NO_2$, –CN) towards the transamidation reaction (**Scheme 3.3**). Aromatic amines showed lower rate of reaction than aliphatic amines due to their lower reactivity (**Scheme 3.4**). The sterically hindered amines undergo transamidation reaction very smoothly and good to excellent yield of product were obtained (**Scheme 3.5**).

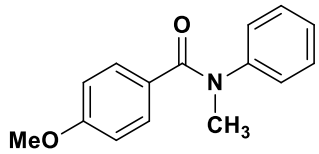
**Scheme 3.3:** $CeCl_3.7H_2O$ catalyzed transamidation of N-$COCF_3$ activated amides with aromatic amines[a]



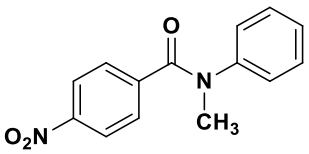

1a-d 2a-i 3.1-3.17



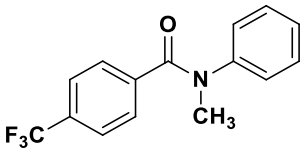
3.1, 86%[b]



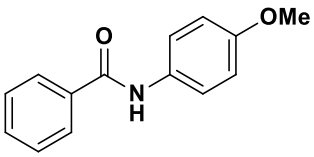
3.2, 85%



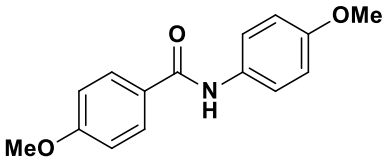
3.3, 88%



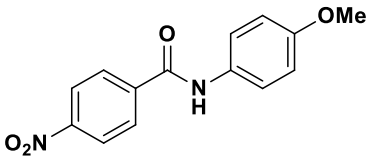
3.4: 85%



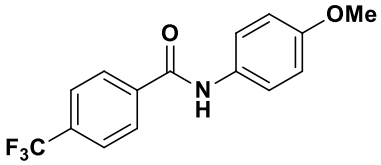
3.5, 90%



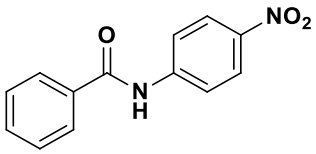
3.6, 84%



3.7, 89%



3.8, 82%



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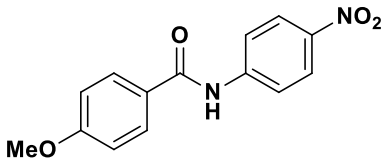
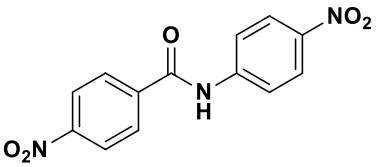
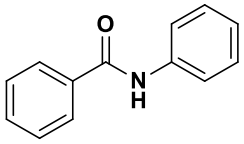


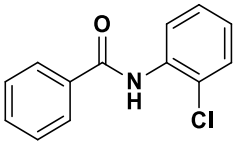
3.10, 82%



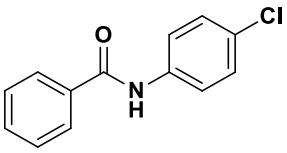
3.11, 85%



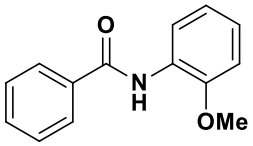
3.12, 90%



3.13, 87%



3.14, 88%



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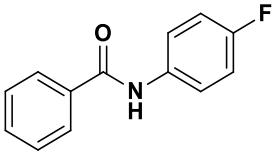
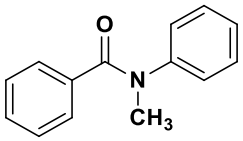


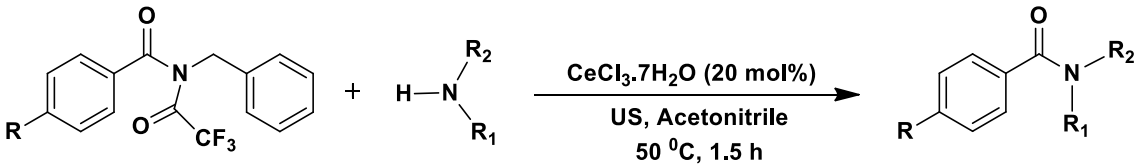
3.16, 85%



3.17, 86%[b]

[a] **Reaction conditions**: Amide (**1**) (1.0 mmol), amine (**2**) (1.2 mmol), $CeCl_3.7H_2O$ (20 mol%) in acetonitrile under ultrasonic irradiation. [b] Isolated yield (%).

**Scheme 3.4:** $CeCl_3.7H_2O$ catalyzed transamidation of N-$COCF_3$ activated amides with aliphatic amines[a]

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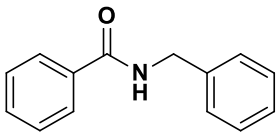
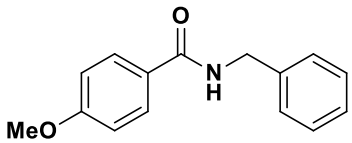
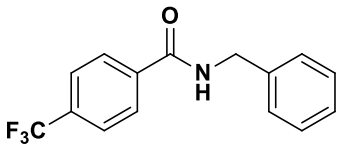


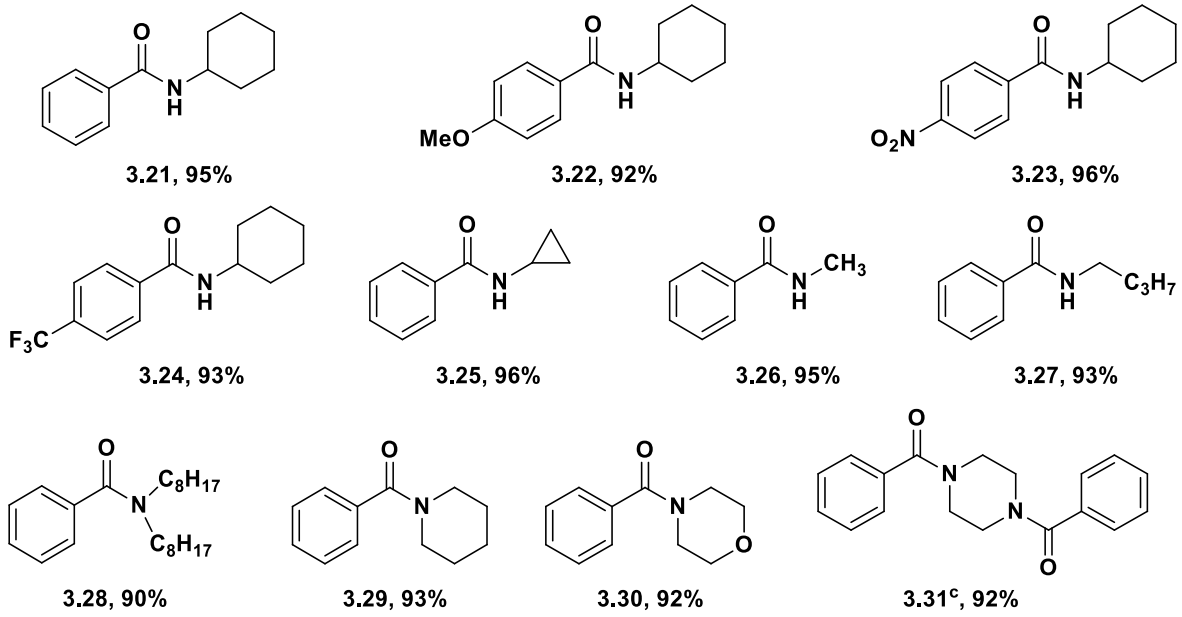
3.18, 95%[b]



3.19, 92%

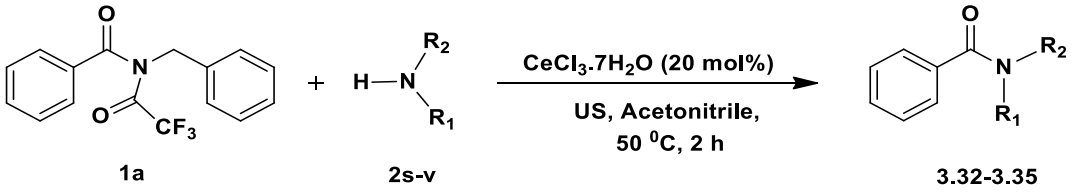


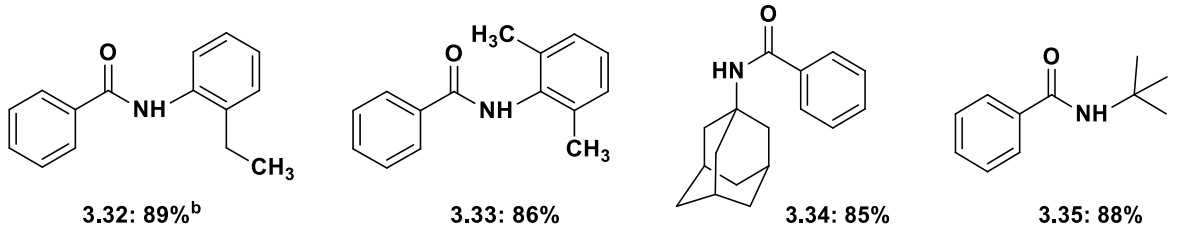
3.20, 90%




[a] **Reaction conditions:** Amide (**1**) (1.0 mmol), amine (**2**) (1.2 mmol), $CeCl_3.7H_2O$ (20 mol%) in acetonitrile under ultrasonic irradiation. [b] Isolated yield (%). [c] **Reaction conditions:** (**1**) (1.0 mmol), (**2**) (2.4 mmol), $CeCl_3.7H_2O$ (20 mol%) in acetonitrile under ultrasond irradiation.

**Scheme 3.5:** $CeCl_3.7H_2O$ catalyzed transamidation of N-$COCF_3$ activated amide with hindered amines[a]




[a] **Reaction conditions**: Amide (**1**) (1.0 mmol), amine (**2**) (1.2 mmol), $CeCl_3.7H_2O$ (20 mol%) in acetonitrile under ultrasonic irradiation. [b] Isolated yield (%).

## 3.3 Mechanistic studies and control experiment

A control experiment was performed using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as radical trapping agent and it was observed that TEMPO does not quenched the reaction this shows that reaction does not proceed through radical intermediate but via nucleophilic pathway. The plausible reaction mechanism of cerium catalyzed transamidation is shown in **Figure 3.2**. The catalytic cycle starts with the activation of carbonyl of *N*-activated amide by the coordination with Ce(III). Amide becomes much more active towards nucleophilic addition and it is attacked by the nucleophilic amine. The proton-exchange and subsequent deamination produces amide and regenerates the catalyst.

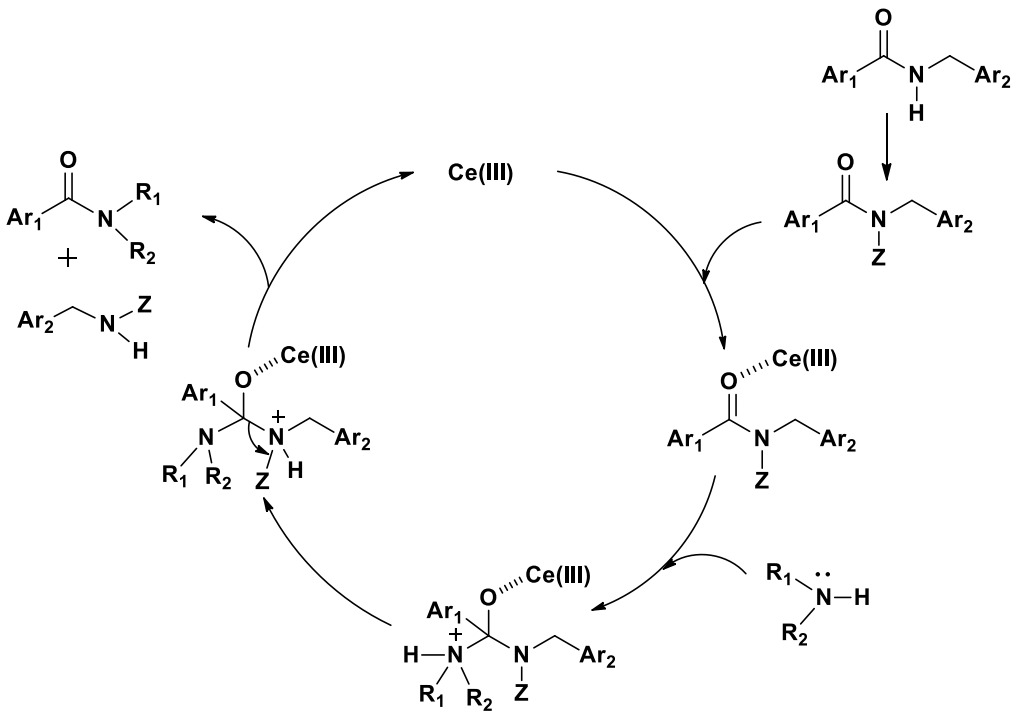



**Figure 3.2:** Plausible mechanism of $CeCl_3.7H_2O$ catalyzed transamidation.

## 3.4 Scalability of the protocol

The scalability of this protocol was tested on the model reaction of N-$COCF_3$ activated *N*-benzylbenzamide (**1a)** (1.53 g, 5.0 mmol) and *N*-methyl aniline **(2a)** (0.64 mL, 6.0 mmol) which gave the desired transamidated product in excellent yield (0.88 g, 84%) under the optimum conditions.

## 3.5 Experimental section

### 3.5.1 General procedure of Cerium(III)-catalyzed transamidation reaction

To a mixture of amide (**1**) (0.10 mmol, 1.0 equiv) and amine (**2**) (0.12 mmol, 1.2 equiv) in acetonitrile (1.0 mL), 20 mol% $CeCl_3.7H_2O$ was added. The reaction mixture was taken in a beaker and irradiated under ultrasonication at 750 W, 50 $^0$C for respective time. The progress of the reaction was monitored by TLC. On completion of reaction, catalyst was filter off. Acetonitrile was evaporated under reduced pressure and reaction mixture was diluted with dichloromethane and washed with water. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to give almost pure product (**3.1**-**3.35**). In case if required recrystallization and column chromatography were performed for further purification.

### 3.5.2 Gram-scale transamidation procedure

Amide (**1**) (5.0 mmol), amine (**2**) (6.0 mmol), 20 mol% $CeCl_3.7H_2O$ and acetonitrile (10.0 mL) were taken in a 50 mL beaker. The reaction mixture was irradiated under ultrasonication at 750 W, 5000 J, 50 $^0$C for respective time. The progress of the reaction was monitored by TLC. After completion of reaction catalyst was filtered off, excess of acetonitrile was evaporated under reduced pressure and pure product was obtained by extracting with dichloromethane followed by water wash.

## 3.6 Analytical data

***N*-Benzyl-*N*-(2,2,2-trifluoroacetyl)benzamide (1a):** White solid: yield 85%; m.p. 40-41 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.65 (t, 3 H), 7.47 (t, 2 H), 7.35 – 7.12 (m, 5 H), 4.98 (s, 2 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 172.42, 134.92, 134.21, 132.74, 129.65, 129.20, 128.99, 128.44, 128.27, 51.03; **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ (ppm): -75.15.

***N*-Methyl-*N*-phenylbenzamide (3.1):** Yellow oil; yield 86%; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.22 – 7.19 (m, 2 H), 7.16 – 7.09 (m, 3 H), 7.09 – 7.01 (m, 3 H), 6.94 (d, 2 H), 3.41 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 170.69, 144.91, 135.94, 129.60, 129.16, 128.71, 127.74, 126.92, 126.51, 38.42.

**4-Methoxy-*N*-methyl-*N*-phenylbenzamide (3.2):** Yellow solid; yield 85%; m.p. 74-75 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.40 (s, 1 H), 8.03 – 7.78 (m, 2 H), 7.71 – 7.40 (m, 2 H), 7.02 – 6.69 (m, 4 H), 3.80 (d, 3 H), 3.73 (d, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$+DMSO-$d_6$) δ (ppm): 164.88, 161.48, 155.39, 131.70, 128.96, 126.94, 121.84, 113.22, 112.90, 112.87, 54.83, 39.50.

***N*-Methyl-4-nitro-*N*-phenylbenzamide (3.3):** Yellow solid; yield 88%; m.p. 110-11 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.95 (d, 2 H), 7.37 (d, 2 H), 7.25 – 7.07 (m, 3 H), 6.96 (d, 2 H), 3.45 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 168.47, 148.06, 143.89, 142.24, 129.67, 129.64, 127.47, 127.04, 123.13, 38.40.

***N*-Methyl-*N*-phenyl-4-(trifluoromethyl)benzamide (3.4):** Yellow solid; yield 85%; m.p. 70-71 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.34 (q, 4 H), 7.25 – 7.05 (m, 3 H), 6.95 (d, 2 H), 3.43 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 169.28, 144.32, 139.55, 131.03, 129.53, 129.10, 128.96, 127.15, 127.02, 124.90, 124.87, 71.91, 38.49.

***N*-(4-Methoxyphenyl)benzamide (3.5):** Green solid; yield 90%; m.p. 155-56 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.85 (d, 3 H), 7.54 (d, 3 H), 7.46 (t, 2 H), 6.89 (d, 2 H), 3.81 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 165.82, 156.76, 135.15, 131.82, 131.13, 128.86, 127.12, 122.28, 114.36, 55.63.

**4-Methoxy-*N*-(4-methoxyphenyl)benzamide (3.6):** Pink solid; yield 84%; m.p. 201-02 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$+DMSO-$d_6$) δ (ppm): 8.99 (s, 1 H), 7.48 (d, 2 H), 7.17 (d, 2 H), 6.47 (d, 2 H), 6.39 (d, 2 H), 3.39 (s, 3 H), 3.32 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$ + DMSO-$d_6$) δ (ppm): 164.88, 161.48, 155.39, 131.70, 128.96, 126.94, 121.84, 113.22, 112.90, 112.87, 54.83.

***N*-(4-Methoxyphenyl)-4-nitrobenzamide (3.7):** Green solid; yield 89%; m.p. 196-97 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.34 (d, 2 H), 8.03 (d, 2 H), 7.79 (s, 1 H), 7.54 (d, 2 H), 6.93 (d, 2 H), 3.83 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 157.33, 140.76, 130.35, 128.35, 124.16, 122.45, 114.55, 55.68.

***N*-(4-Methoxyphenyl)-4-(trifluoromethyl)benzamide (3.8):** Yellow oil; yield 82%; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.98 (d, 2 H), 7.76 (d, 2 H), 7.71 (s, 1 H), 7.54 (d, 2 H), 6.93 (d, 2 H), 3.83 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 127.61, 122.35, 114.50, 55.68.

***N*-(4-Nitrophenyl)benzamide (3.9):** White solid; yield 84%; m.p. 197-98 $^0$C; **$^1$H NMR** (500 MHz, DMSO–$d_6$) δ (ppm): 10.82 (s, 1 H), 8.27 (d, 2 H), 8.06 (d, 2 H), 7.97 (d, 2 H), 7.64 (t,1 H), 7.56 (t, 2 H); **$^{13}$C NMR** (126 MHz, DMSO–$d_6$) δ (ppm): 166.39, 145.45, 142.60, 134.24, 132.35, 128.67, 128.01, 124.92, 120.00, 119.92.

**4-Methoxy-*N*-(4-nitrophenyl)benzamide (3.10):** Yellow solid; yield 82%; m.p. 184-85 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.25 (d, 1 H), 8.14 (s, 1 H), 8.10 – 8.05 (m, 2 H), 7.88 – 7.83 (m, 2 H), 7.03 – 6.91 (m, 2 H), 6.62 (d, 1 H), 3.89 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 164.77, 163.23, 152.61, 144.23, 132.98, 129.30, 126.50, 125.28, 119.48, 114.35, 114.30, 113.51, 55.69.

**4-Nitro-*N*-(4-nitrophenyl)benzamide (3.11):** Yellow solid; yield 85 %; m.p. 273-74 $^0$C; **$^1$H NMR** (500 MHz, DMSO–$d_6$) δ (ppm): 11.09 (s, 1 H), 8.43 – 8.36 (m, 2 H), 8.32 – 8.26 (m, 2 H), 8.21 (d, 2 H), 8.06 (d, 2 H); **$^{13}$C NMR** (126 MHz, DMSO–$d_6$) δ (ppm): 164.67, 149.44, 144.91, 142.84, 139.81, 129.47, 124.82, 123.61, 120.09.

***N*-Phenylbenzamide (3.12):** White solid: yield 90%; m.p. 163-64 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.87 (d, 3 H), 7.64 (d, 2 H), 7.55 (t, 1 H), 7.48 (t, 2 H), 7.37 (t, 2 H), 7.15 (t, 1 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 165.90, 138.06, 135.16, 131.99, 129.25, 128.94, 127.16, 124.73, 120.35.

***N*-(2-Chlorophenyl)benzamide (3.13):** White solid; yield 87%; m.p. 96-97 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.57 (d, 1 H), 8.45 (s, 1 H), 7.92 (d, 2 H), 7.58 (t, 1 H), 7.52 (t, 2 H), 7.41 (dd, 1 H), 7.37 – 7.30 (m, 1 H), 7.13 – 7.04 (m, 1 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 165.42, 134.89, 134.77, 132.33, 129.17, 129.09, 128.03, 127.23, 124.89, 123.17, 121.65, 77.41, 77.16, 76.91.

***N*-(4-Chlorophenyl)benzamide (3.14):** White solid; yield 88%; m.p. 195-96 $^0$C; **$^1$H NMR** (500 MHz, DMSO–$d_6$) δ (ppm): 10.38 (s, 1 H), 7.93 (d, 2 H), 7.81 (d, 2 H), 7.60 (t, 1 H), 7.53 (t, 2 H), 7.41 (d, 2 H); **$^{13}$C NMR** (126 MHz, DMSO–$d_6$) δ (ppm): 165.77, 138.10, 134.71, 131.89, 128.66, 128.58, 127.77, 127.43, 122.03, 121.93.

***N*-(2-Methoxyphenyl)benzamide (3.15):** Brown solid; yield 89%; m.p. 59-60 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.56 (s, 1 H), 8.54 (dd, 1 H), 7.93 – 7.85 (m, 2 H), 7.58 – 7.46 (m, 3 H), 7.10 – 7.01 (m, 2 H), 6.92 (dd, 1 H), 3.92 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 165.40, 148.28, 135.48, 131.82, 128.89, 127.94, 127.19, 124.01, 121.35, 119.99, 110.07, 55.95.

***N*-(4-Fluorophenyl)benzamide (3.16):** White solid; yield 85%; m.p. 186-87 $^0$C; **$^1$H NMR** (500 MHz, DMSO–$d_6$) δ (ppm): 10.32 (s, 1 H), 7.94 (d, 2 H), 7.85 – 7.83 (m, 2 H), 7.59 (t, 1 H), 7.53 (t, 2 H), 7.19 (t, 2 H); **$^{13}$C NMR** (126 MHz, DMSO–$d_6$) δ (ppm): 165.58, 159.38, 157.47, 135.48, 134.80, 131.77, 128.55, 127.72, 122.30, 122.24, 115.40, 115.22.

***N*-(4-Cyanophenyl)benzamide (3.17):** Yellow solid; yield 86%; m.p. 169-70 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.03 (s, 1 H), 7.88 (d, 1 H), 7.80 (d, 1 H), 7.76 – 7.63 (m, 3 H), 7.63 – 7.43 (m, 2 H), 7.36 (t, 2 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 173.15, 142.12, 134.28, 133.52, 133.14, 132.66, 129.48, 129.15, 128.94, 128.39, 127.24, 120.02.

***N*-Benzylbenzamide (3.18):** White solid; yield 95%; m.p. 104-05 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.79 (d, 2 H), 7.50 (t, 1H), 7.43 (t, 2 H), 7.40 – 7.27 (m, 5 H), 6.40 (s, 1 H), 4.66 (d, 2 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 167.49, 138.31, 134.56, 131.71, 128.96, 128.76, 128.09, 127.81, 127.09, 44.32.

***N*-Benzyl-4-methoxybenzamide (3.19):** White solid; yield 92%; m.p. 124-26 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.10 (d, 1 H), 7.76 (d, 2 H), 7.35 (d, 4 H), 6.91 (d, 2 H), 6.37 (s, 1 H), 4.63 (d, 2 H), 3.84 (s, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 167.00, 164.72, 162.37, 138.53, 132.97, 128.90, 128.05, 127.70, 126.78, 121.41, 114.27, 113.90, 55.54, 44.22.

***N*-Benzyl-4-(trifluoromethyl)benzamide (3.20):** White solid; yield 90%; m.p. 167-68 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.59 (m, 3 H), 7.51 – 7.35 (m, 3 H), 7.29 (t, 2 H), 7.21 – 7.17 (m, 1 H), 4.98 (s, 2 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 134.91, 134.21, 129.65, 129.20, 128.99, 128.86, 128.44, 128.27, 128.13, 127.12, 51.03.

***N*-Cyclohexylbenzamide (3.21):** White solid; yield 95%; m.p. 146-47 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.75 (d, 2 H), 7.48 (t, 1 H),7.42 (t, 2 H), 6.00 (s, 1 H), 4.07 – 3.91 (m, 1 H), 2.03 (d, 2 H), 1.76 (d, 2 H), 1.66 (d, 1 H), 1.43 (q, 2 H), 1.24 (q, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 166.78, 135.24, 131.37, 128.65, 126.95, 48.80, 33.37, 25.71, 25.04.

***N*-Cyclohexyl-4-methoxybenzamide (3.22):** White solid; yield 92%; m.p. 159-61 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.63 (m, 2 H), 6.96 – 6.85 (m, 2 H), 5.90 (d, 1 H), 3.84 (s, 3 H), 2.07 – 1.99 (m, 2 H), 1.81 – 1.71 (m, 2 H), 1.68 – 1.61 (m, 1 H), 1.49 – 1.37 (m, 2 H), 1.28 – 1.17 (m, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 166.24, 162.12, 128.72, 127.53, 113.80, 96.26, 88.58, 55.53, 48.70, 33.46, 25.75, 25.08.

***N*-Cyclohexyl-4-nitrobenzamide (3.23):** White solid; yield 96%; m.p. 197-98 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.28 (d, 2 H), 7.91 (d, 2 H), 6.02 (s, 1 H), 4.02 – 3.90 (m, 1 H), 3.84 (s, 3 H), 2.04 – 2.01 (m, 2 H), 1.85 – 1.74 (m, 2 H), 1.72 – 1.64 (m, 1 H), 1.47 – 1.38 (m, 2 H), 1.26 – 1.16 (m, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 164.73, 149.64, 140.83, 128.19, 123.93, 49.38, 33.27, 25.62, 25.00.

***N*-Cyclohexyl-4-(trifluoromethyl)benzamide (3.24):** White solid; yield 93%; m.p. 182-83 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.85 (d, 2 H), 7.68 (d, 2 H), 6.06 (s, 1 H), 4.28 – 3.78 (m, 1 H), 2.04 (d, 2 H), 1.78 – 1.75 (m, 2 H), 1.43 (q, 2 H), 1.32 – 1.15 (m, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 165.50, 138.54, 127.47, 125.71, 125.68, 125.65, 49.15, 33.30, 25.65, 25.02.

***N*-Cyclopropylbenzamide (3.25):** White solid; yield 96%; m.p. 100-01 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.67 (d, 2 H), 7.41 – 7.30 (m, 3 H), 6.39 (s, 1 H), 2.83 – 2.81 (m, 1 H), 0.78 (s, 2 H), 0.55 (s, 2 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 169.07, 134.54, 131.56, 128.62, 126.98, 23.25, 6.85.

***N*-Methylbenzamide (3.26):** Yellow solid; yield 95%; m.p. 82-83 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.71 – 7.68 (m, 2 H), 7.44 – 7.38 (m, 1 H), 7.37 – 7.29 (m, 2 H), 6.36 (s, 1 H), 2.92 (d, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 168.45, 134.72, 131.44, 128.63, 126.96, 26.94.

***N*-Butylbenzamide (3.27):** Yellow oil; yield 93%; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.79 – 7.73 (m, 2 H), 7.51 – 7.46 (m, 1 H), 7.42 (t, 2 H), 6.16 (s, 1 H), 3.46 (q, 2 H), 1.64 – 1.55 (m, 2 H), 1.48 – 1.36 (m, 2 H), 0.96 (t, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 167.68, 135.01, 131.44, 130.72, 129.03, 128.68, 126.95, 39.94, 31.89, 20.30, 13.93.

***N, N*-Dioctylbenzamide (3.28):** Dark brown oil; yield 90%; **$^1$H NMR (**500 MHz, $CDCl_3$) δ (ppm): 7.38 – 7.33 (m, 5 H), 3.47 (s, 2 H), 3.17 (s, 2 H), 1.48 – 1.11 (m, 22 H), 0.88 (bs, 8 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 171.78, 137.56, 129.12, 128.47, 126.59, 49.15, 44.89, 31.92, 29.41, 29.20, 27.68, 27.23, 26.64, 22.77, 19.30, 14.22.

**Phenyl(piperidin-1-yl)methanone (3.29):** Yellow oil; yield 93%; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.39 (s, 5 H), 3.72 (s, 2 H), 3.34 (s, 2 H), 1.68 (s, 4 H), 1.52 (s, 2 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 170.46, 136.64, 129.48, 128.53, 126.91, 48.90, 43.24, 24.73.

**Morpholino(phenyl)methanone (3.30):** Yellow soild; yield 92%; m.p. 93-94 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.48 – 7.36 (m, 5 H), 4.15 – 3.22 (m, 8 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 170.61, 135.45, 130.03, 128.71, 127.23, 67.05.

**Piperazine-1,4-diylbis(phenylmethanone) (3.31):** White solid; yield 92%; m.p. 194-95 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.42 (s, 10 H), 3.64 (d, 8 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 170.81, 135.25, 130.25, 128.79, 127.19, 47.64, 42.51.

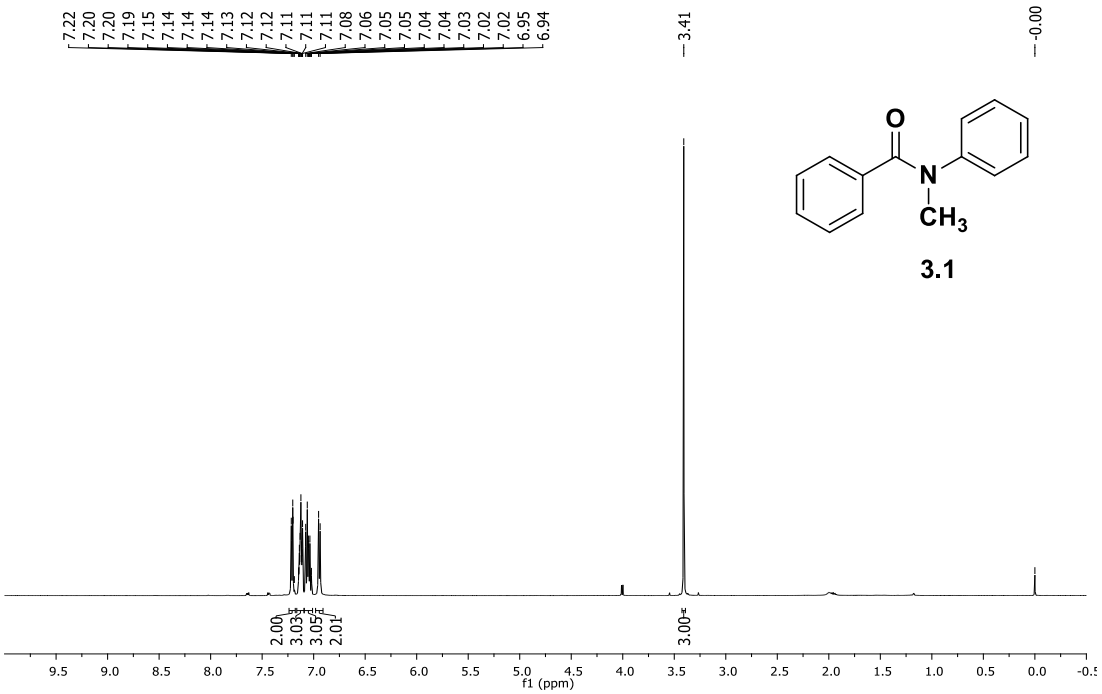
***N*-(2-Ethylphenyl)benzamide (3.32):** White solid; yield 89%; m.p. 159-60 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.94 (d, 1 H), 7.88 (d, 2 H), 7.74 (s, 1 H), 7.57 (t, 1 H), 7.50 (t, 2 H), 7.32 – 7.23 (m, 2 H), 7.17 (t, 1 H), 2.69 (q, 2 H), 1.28 (t, 3 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 165.96, 135.51, 135.19, 135.10, 131.91, 128.93, 128.71, 127.15, 126.88, 125.85, 124.02.

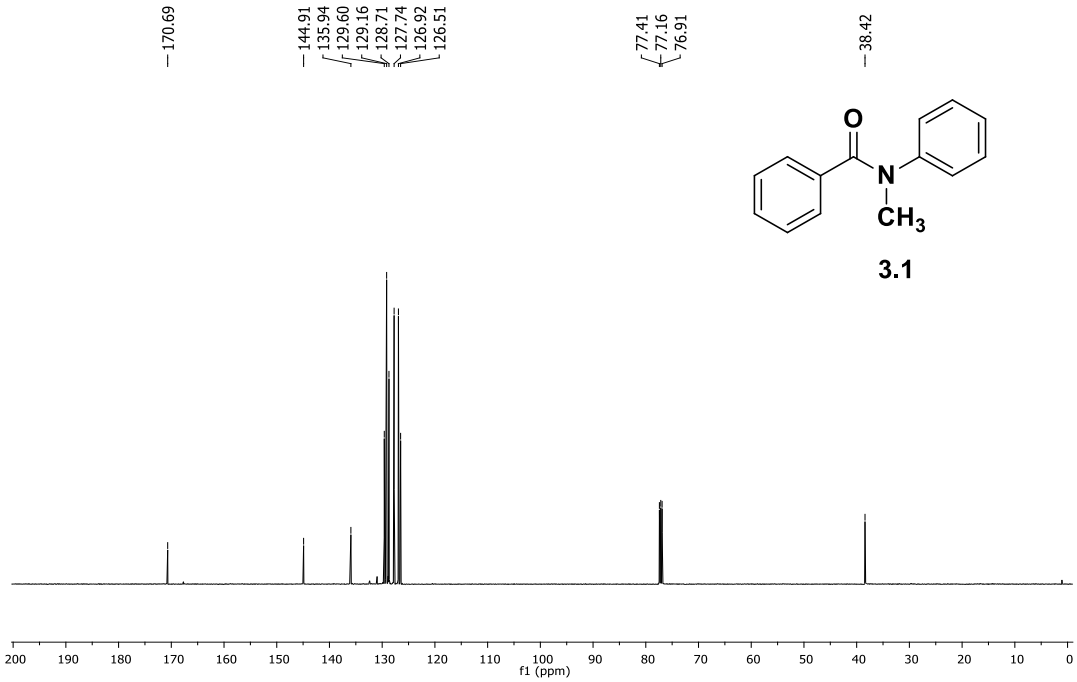
***N*-(2,6-Dimethylphenyl)benzamide (3.33):** White solid; yield 86%; m.p. 168-69 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.93 (d, 2 H), 7.57 (t, 1 H), 7.50 (t, 2 H), 7.41 (s, 1 H), 7.19 – 7.09 (m, 3 H), 2.29 (s, 6 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 166.06, 135.72, 134.66, 133.98, 131.97, 128.93, 128.45, 127.61, 127.35, 18.64.

***N*-((3s,5s,7s)-Adamantan-1-yl)benzamide (3.34):** White solid; yield 85%; m.p. 144-45 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.76 – 7.66 (m, 2 H), 7.48 – 7.44 (m, 1 H), 7.40 (t, 2 H), 5.80 (s, 1 H), 2.13 (s, 9 H), 1.71 (d, 6 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 166.80, 162.51, 136.19, 134.69, 131.17, 130.72, 129.02, 129.00, 128.59, 126.84, 52.42, 41.82, 36.52, 29.64.

***N*-(*tert*-Butyl)benzamide (3.35):** White solid; yield 88%; m.p. 135-36 $^0$C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.72 (dd, 2 H), 7.50 – 7.45 (m, 1 H), 7.41 (t, 2 H), 5.94 (s, 1 H), 1.48 (s, 9 H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ (ppm): 167.06, 136.07, 131.23, 128.63, 126.83, 51.75, 29.02.

## 3.7 Spectral data of product (3.1)



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