JOC The Journal of Organic Chemistry

Article

Chemo-Selective Synthesis of Aryl Ketones from Amides and Grignard Reagents via C(O)-N Bond Cleavage Under Catalyst-free Condition

Popuri Sureshbabu, sadaf azeez, Nalluchamy Muniyappan, Shahulhameed Sabiah, and Jeyakumar Kandasamy

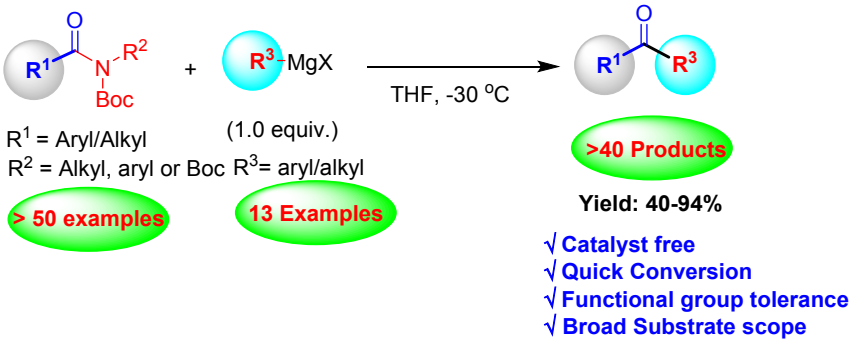
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01699 • Publication Date (Web): 22 Aug 2019

Chemo-Selective Synthesis of Aryl Ketones from Amides and Grignard Reagents *via C(O)-N* Bond Cleavage Under Catalyst-free Condition

Popuri Sureshbabu,[a#] Sadaf Azeez,[a#] Nalluchamy Muniyappan[b] Shahulhameed Sabiah[b] and Jeyakumar Kandasamy[a]*

[a]Department of Chemistry, Indian Institute of Technology (BHU), Varanasi, Uttar Pradesh-221005.
[b]Department of Chemistry, Pondicherry University, Pondicherry-605014

TOC



Abstract:

Conversion of a wide range of *N*-Boc amides into aryl ketones was achieved with Grignard reagents *via* chemoselective *C*(*O*)-*N* bond cleavage. The reactions proceeded under catalyst-free condition with different aryl, alkyl and alkynyl Grignard reagents. α-Ketoamide was successfully converted into aryl diketones while α,β-unsaturated amide undergoes 1,4-addition followed by *C*(*O*)-*N* bond cleavage to provide diaryl propiophenones. *N*-Boc amides displayed higher reactivity than Weinreb amides with Grignard reagents. Broad substrate scope, excellent yields and quick conversion are important features of this methodology.

Introduction

Aryl ketones are not only important starting materials but also structural components of various drugs and bioactive molecules (Figure 1).[1] Aryl ketones are typically prepared by Friedel–Crafts acylation reactions[2] or by the oxidation of secondary alcohols.[3] Amide is one of the key functional groups in organic chemistry that present in biomolecules (e.g. proteins), natural products and pharmaceutics.[4] Recently, the activation of amides has emerged as a tool for the chemo-selective synthesis of various biologically relevant molecules *via C*(*O*)-*N* bond cleavage.[5]

In this context, the transformation of amides into ketones catalyzed by transition metals has received significant interest in organic synthesis.[6-9] Garg and co-workers demonstrated the conversion of twisted amides (*i.e.* *N*-Boc and *N*-tosyl amides) into ketonic compounds with organozinc and organoboron reagents using nickel catalysts.[7] Extensive research work on the conversion of amides to ketones was carried out by the Szostak research group which focused on the palladium catalyzed coupling reaction of aryl boronic acids not only with *N*-Boc but also various structurally distorted amides.[8] Moreover, Szostak *et al*. also demonstrated the nickel catalyzed organozinc mediated transformation of *N*-Boc amides into aryl ketones.[9]

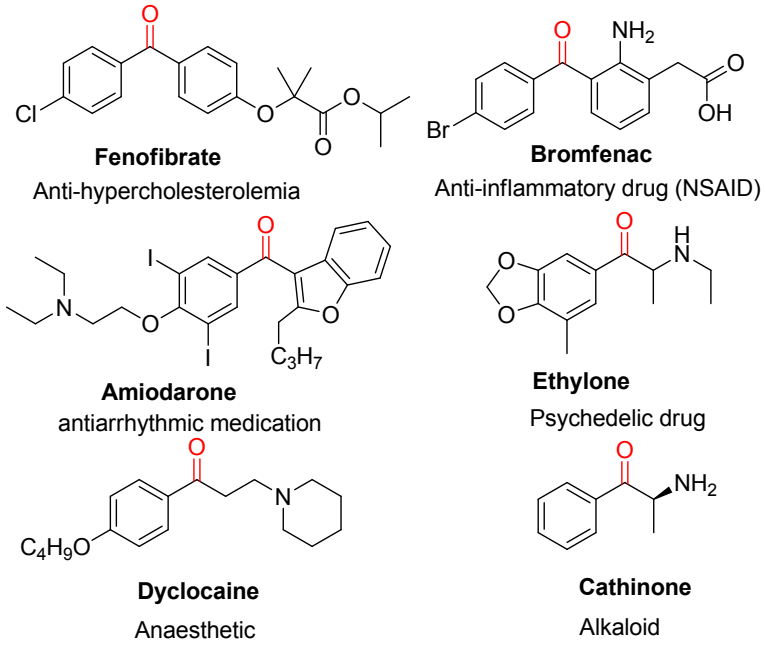
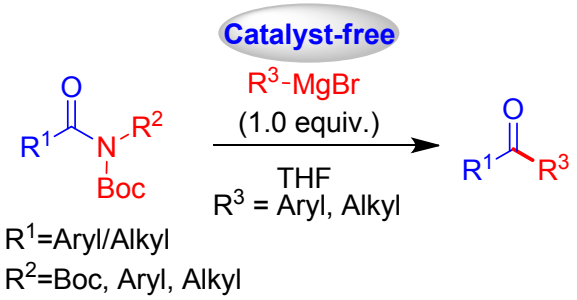


Figure 1. Biologically relevant ketonic compounds

Grignard reagents are powerful aryl donors utilized in many cross-coupling reactions.[10] The reaction of Grignard reagents with Weinreb amides is well known in organic synthesis and provides ketones in good to excellent yields.[11] Synthesis of aryl ketones from structurally distorted *N*-acylazetidines and Grignard reagents was demonstrated by Szostak *et al.*[12] However, unlike organolithium compounds, aryl Grignard reagents showed less reactivity, requiring elevated reaction temperature *i.e.* up to 60 °C. Recently, chromium catalyzed Kumada arylation of unprotected secondary amides to ketone with Grignard reagents was demonstrated by Zeng *et al.* in the presence of TMS-Cl.[13] This method is attractive; however, it requires four equivalents of Grignard reagents. In 1989, Giovannini *et al.* investigated the ring opening reactions of *N*-acyl and carbomate (e.g. tBuC(O), Cbz, Boc) protected lactam with Grignard reagents.[14] However,

the scope and limitations of *N*-protected acyclic amides with Grignard reagent were not investigated.[15] Nevertheless, establishing such methods may allow direct access to aryl-aryl, aryl-alkyl ketones in a simple manner from amides. Our research group is focused on the chemistry of *N*-nitrosamines[16] and recently demonstrated the transamidation of secondary amides using *tert*-butyl nitrite.[16a] In continuation of this work, here we report the synthesis of aryl ketones from *N*-Boc protected amides and Grignard reagents under catalyst-free condition (Scheme 1).

Scheme 1. Conversion of *N*-Boc amides into ketones.

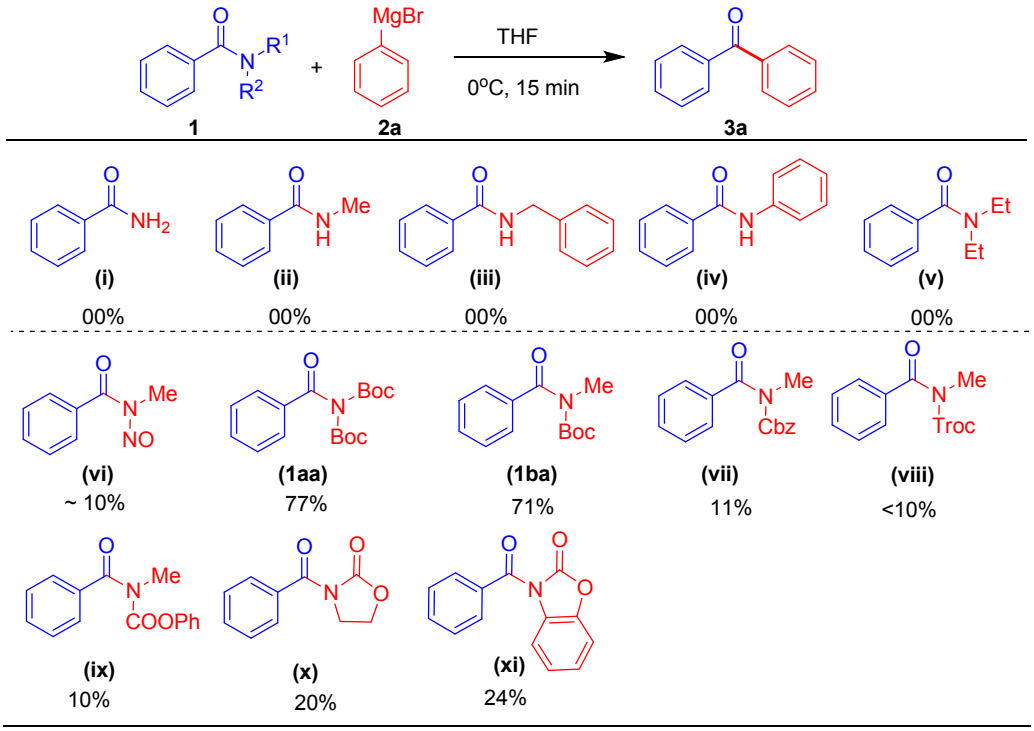


Results and Discussion

At the outset, the selective *C*(*O*)-*N* bond cleavage of different unprotected as well as protected/activated amides with Grignard reagents was investigated (Scheme 2). Different benzamides were subjected to the Grignard reactions with phenylmagnesium bromide (1.0 equiv.) in THF at 0 °C. In fact, no reaction was observed with unprotected primary as well as secondary amides such as benzamide, *N*-methyl, *N*-benzyl and *N*-phenyl benzamides (Scheme 2, **i-iv**). Moreover, tertiary amide such as *N,N*-diethyl benzamide (**v**) also failed to provide the desired ketone. However, *N*-nitroso *N*-methyl benzamide (**vi**) gave the desired diphenyl ketone (**3a**) in a trace amount. It is noteworthy that among the different activated amides, *N*-Boc protected amides have shown excellent reactivity not only in coupling reactions but also in transamidation and transesterification reactions under mild conditions.[17] Moreover, *N*-Boc protected amides can be easily and directly achieved from unprotected primary and secondary amides in a single step with good yields. Therefore, the Grignard reaction was performed with *N*-Boc protected primary and secondary benzamides (**1aa** and **1ba**). To our delight, the coupling reaction underwent smoothly with both of these amides while *N,N*-di-Boc benzamide (**1aa**) gave the desired product in 77% yield. Further, benzamides with different *N*-protecting groups such as

Cbz, Troc, phenyl carbamate, oxazolidine and benzoxazolone was subjected to the *C*(*O*)-*N* bond cleavage with phenyl magnesium bromide (Scheme 2, **vi-xi**). Unfortunately, all these amides gave the desired ketone **3a** in low yields.

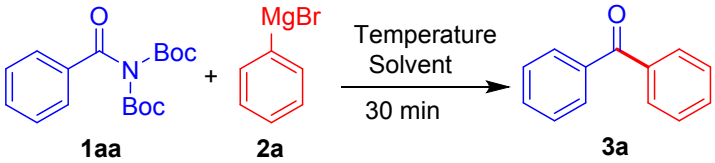
Scheme 2. Reaction of different amides with phenylmagnesium bromide.[a,b]



[a]Conditions: Substrate (1 mmol) and PhMgBr (**2a**) (1.0 equiv.) in THF (3 mL) at 0 °C for 15 min. [b]Isolated yield.

Seeking further optimization, the conversion of *N,N*-di-Boc benzamide (**1aa**) into diphenyl ketone was investigated at different temperatures in THF (Table 1, entries 1-7). It was observed that the reaction proceeds smoothly at -30 °C, providing the desired product in 93% yield within 30 min (Table 1, entry 5). However, the other solvents including diethyl ether and toluene were found to be less suitable for the reactions, providing lower yields (Table 1, entries 8 and 9). Moreover, by increasing the amount of phenylmagnesium bromide from 1.0 equiv. to 1.2, 1.5 and 2.0 equiv. did not show any significant change in the yield (Table 1, entries 10-12) . Overall, the optimization study indicated that the transformation of *N*-Boc amides into arylketones can be efficiently achieved with 1.0 equiv. of Grignard reagent at -30 °C (Table 1, entry 5). The attractive features of this methodology such as catalyst-free condition, excellent yield and quick conversion led us to further explore its potential.

Table 1. Optimized condition.[a]



1aa **2a** **3a**

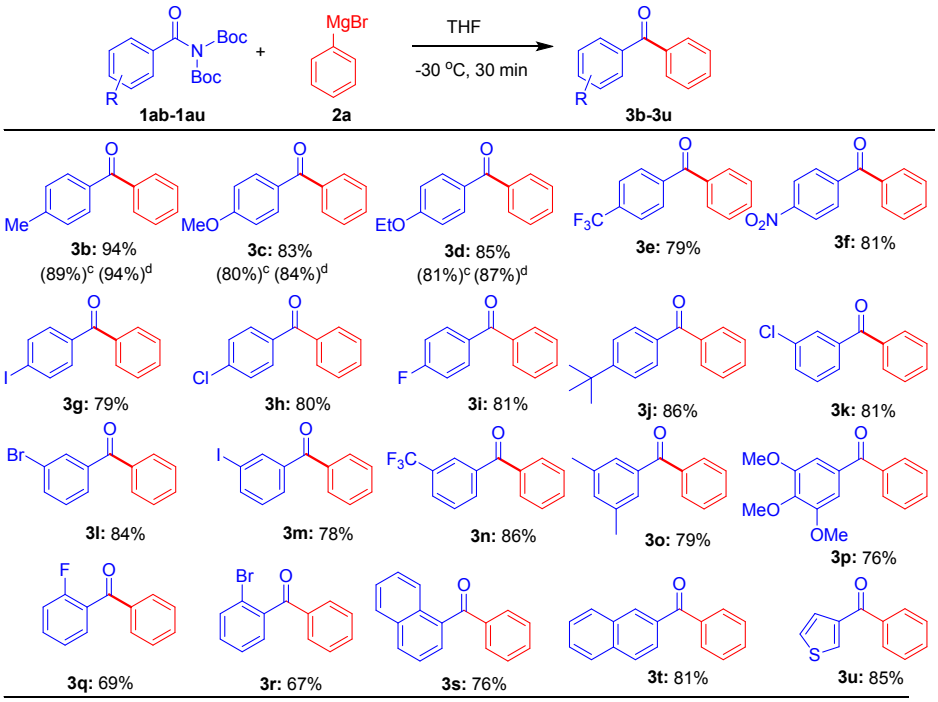
Entry	Solvent	Temp. (°C)	PhMgBr (equiv.)	Yield (%)[b]
1	THF	25	1.0	69
2	THF	~5	1.0	74
3	THF	-10	1.0	80
4	THF	-20	1.0	84
5	THF	-30	1.0	93
6	THF	-50	1.0	65
7	THF	-78	1.0	63
8	Toluene	-30	1.0	56
9	Et_2O	-30	1.0	71
10	THF	-30	1.2	93
11	THF	-30	1.5	89
12	THF	-30	2.0	86

[a]Conditions: Substrate (**1aa**: 321 mg, 1 mmol) and PhMgBr (**2a:** 1 mL, 1 mmol) in solvent (3 mL) at different temperature. [b]Isolated yield.

With optimized conditions in hand, the substrate scope was investigated with a wide range of functionalized *N,N*-di-Boc benzamides in the presence of phenylmagnesium bromide (Scheme 3). To our delight, *N,N*-di-Boc benzamides bearing electron donating groups (e.g. methyl, OMe, OEt, *tert*-butyl) and electron withdrawing groups (e.g. halogens, nitro, trifluoromethane, etc.) at the *para*-position underwent *C*(*O*)-*C* bond formation smoothly and provided the corresponding unsymmetrical diaryl ketones (**3b-3j)** in good to excellent yields. To identify the general applicability of the reaction, we have investigated the preparation of **3b-3d** at standard cooling bath temperatures i.e. -20 °C and -78 °C. It was observed that at -20 °C the reactions proceed smoothly and provides the desired products in comparable yields or slightly lower yields within 30 minutes. On the other hand, at -78 °C the reactions were quite slow and required longer time (6 h) to obtain the desired products in comparable or slightly better yields. Further we have investigated the coupling reactions of *meta*-substituted amides, sterically hindered *ortho*-substituted amides, as well as naphthyl amides under optimized conditions (*i.e.* at -30 °C). These activated amides were successfully transformed into corresponding ketones (**3k-3t)** in the

presence of phenylmagnesium bromide in 67-86% yields. Further to our delight, heterocyclic amide such as *N,N*-di-Boc 2-thiophenecarboxamide also participated in the coupling reaction very efficiently to yield the desired ketone (**3u**) in 85% yield.

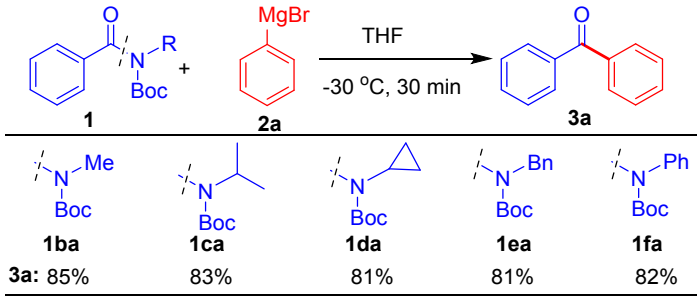
Scheme 3. Reaction with *N,N*-di-Boc activated amides with PhMgBr.[a,b]



[a]Conditions: Substrate (1 mmol) and PhMgBr (**2a**) (1 mL, 1.0 equiv.) in THF (3 mL) at -30 °C for 30 min. [b]Isolated yield. [c]Reactions were performed at -20 °C for 30 min. [d]Reactions were performed at -78 °C for 6 h.

Further, we have investigated the coupling reactions of different *N*-Boc protected secondary benzamides including *N*-methyl, *N*-*iso*-propyl, *N*-cyclopropyl, *N*-benzyl and *N*-phenyl benzamides (**1ba-1fa**) with phenylmagnesium bromide under optimized condition (Scheme 4). All these activated amides were successfully transformed into diphenyl ketone in 81-85% yield.

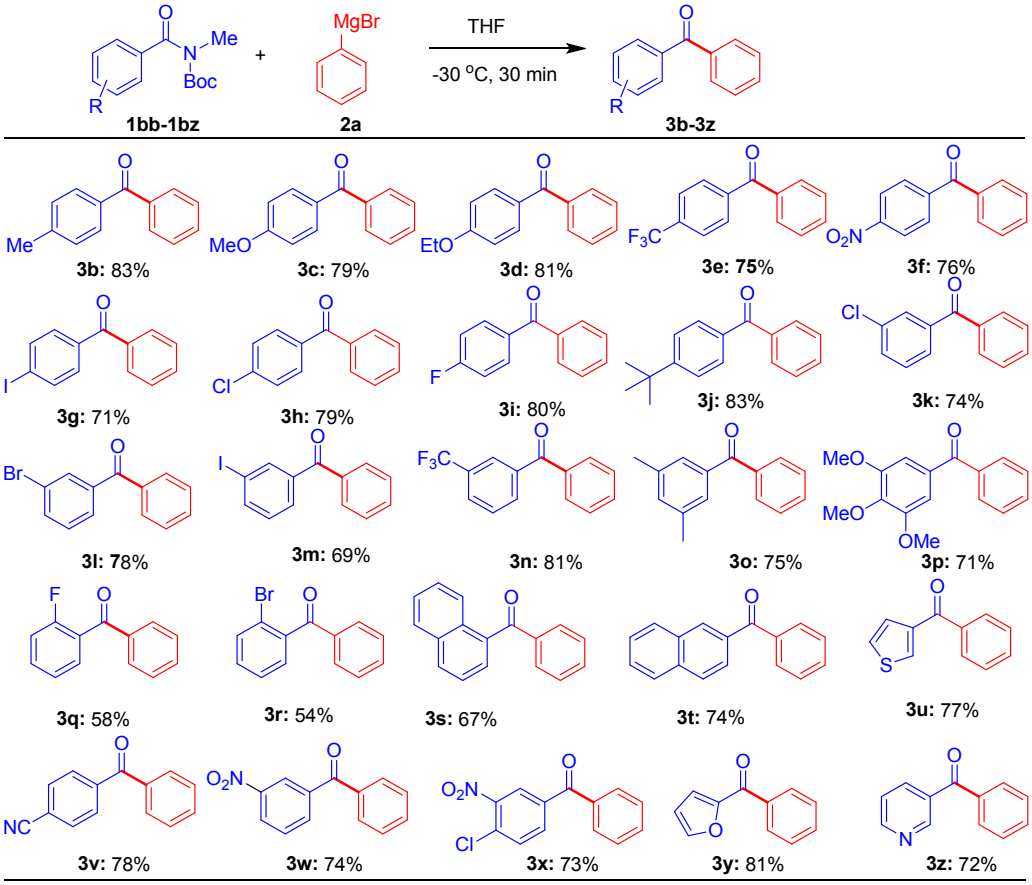
Scheme 4. Reaction of PhMgBr with different *N*-substituted benzamides.[a,b]



[a]Conditions: Substrate (1 mmol) and PhMgBr (**2a**) (1 mL, 1.0 equiv.) in THF (3 mL) at -30 °C for 30 min. [b]Isolated yield.

Subsequently, to investigate the scope of the methodology, a different *N*-Boc protected secondary aryl amides were subjected to the coupling reaction with phenylmagnesium bromide under optimized conditions (Scheme 5). To our delight, similar to *N,N*-di-Boc amides, *N*-Boc *N*-methyl benzamides as well as *N*-Boc *N*-methyl heterocyclic amides were also participated in the coupling reaction very efficiently to yield the corresponding unsymmetrical diaryl ketones **3b-3z** in 54-83% yield.

Scheme 5. Synthesis of aryl ketones: Scope of *N*-Boc benzamides.[a,b]

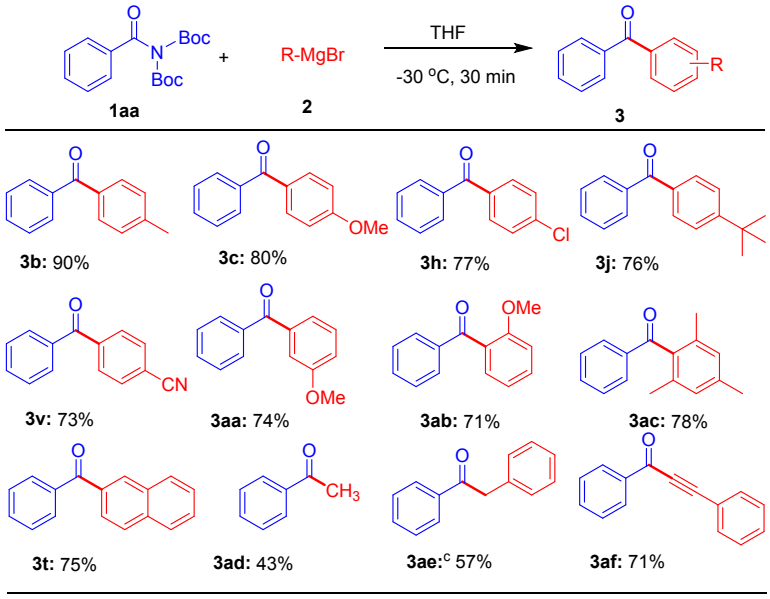


[a]Conditions: Substrate (1 mmol) and PhMgBr (**2a**) (1 mL, 1.0 equiv.) in THF (3 mL) at -30 °C for 30 min. [b]Isolated yield.

From Scheme 3 and 5, it is clear that the electronic effect of substituents on the aryl ring (i.e. electron donating and withdrawing groups) is less significant in terms of reaction progress and the yield. However, sterically hindered *ortho*-substituted amides gave relatively lesser yields of the desired ketones (e.g. **3q-3r**). It is also interesting to note that nitrile group as well as halo-substituents (e.g. I, Br, etc.) on the aryl ring were well tolerated during the coupling reactions.

On the other hand, amides with different *N*-substituents provided diphenyl ketone in comparable yields (Scheme 4) indicating the broad scope of the current methodology.

Scheme 6. Synthesis of ketones from *N,N*-diBoc benzamide: Scope of Grignard Reagents.[a,b]

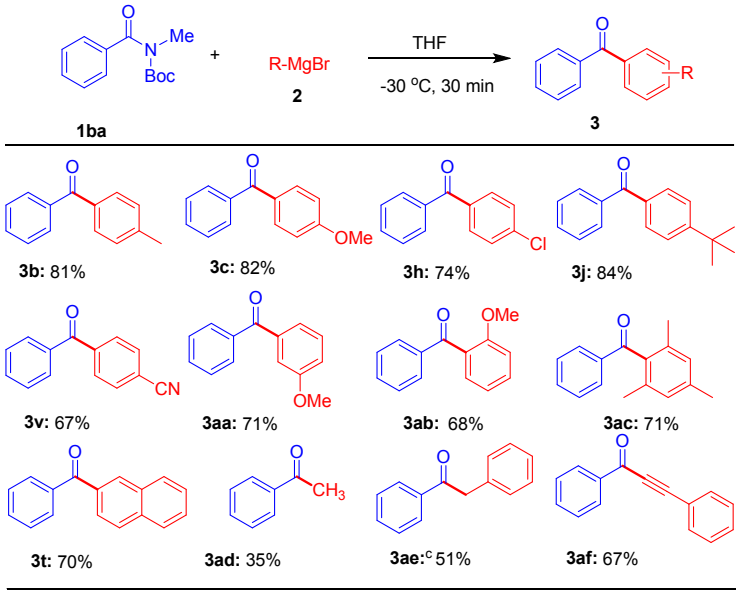


[a]Conditions: Substrate (**1aa**: 321 mg, 1 mmol) and RMgBr (1.0 equiv.) in THF (3 mL) at -30 °C for 30 min. [b]Isolated yield. [c]Benzyl magnesium chloride was used.

Having explored the scope of different amides, *N,N*-di-Boc benzamide (**1aa**) was subjected to the coupling reaction with a wide range of Grignard reagents including aryl, benzyl, alkyl and alkynyl magnesium halides (Scheme 6). It was observed that the electron donating and withdrawing group functionalized aryl magnesium bromides reacted with *N,N*-di-Boc benzamide and gave the corresponding diaryl ketones (Scheme 6, **3b**, **3c**, **3h**, **3j**, **3v**, **3aa-3ac** and **3t**) in 43-90% yields. Notably, strongly electron withdrawing group functionalized 4-cyano phenylmagnesium bromide also participated in the coupling reaction and provided the desired ketone in 73% yield. Moreover, sterically hindered *ortho*-substituted Grignard reagents (i.e. 2-methoxyphenylmagnesium bromide and 2,4,6-tri-methylphenylmagnesium bromide) as well as 2-naphthylmagnesium bromide were successfully coupled with *N*-Boc *N*-methyl benzamide in excellent yields. Further, the amide **1aa** was subjected to the coupling reaction with alkyl and alkynyl Grignard reagents such as methyl, benzyl and phenylethynylmagnesium halides under optimized conditions. All these reactions gave the desired ketones **3ad-3af** in good to moderate yields.

After exploring the reactions of *N*,*N*-di-Boc benzamide with different Grignard reagents, the scope of *N*-Boc protected secondary amide was investigated. *N*-Methyl *N*-Boc benzamide (**1ba**) was subjected to the coupling reactions with different Grignard reagents under optimized conditions (Scheme 7). To our delight, diaryl ketones were obtained in 35-84% yields indicating the broad scope of the developed methodology.

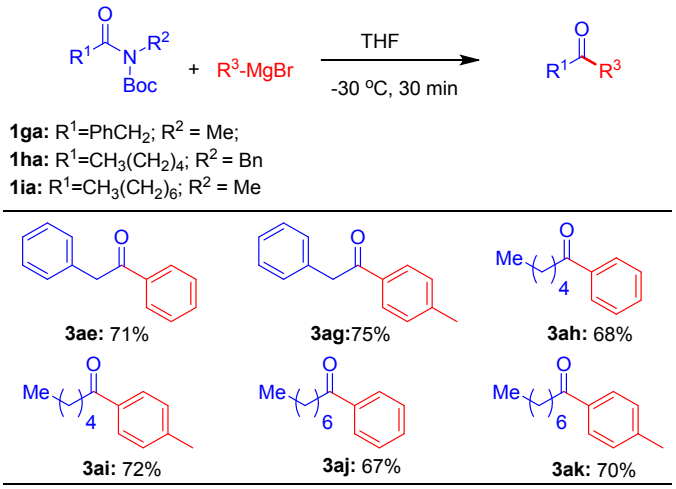
Scheme 7. Synthesis of ketones from *N*-methyl *N*-Boc benzamide: Scope of Grignard Reagents.[a,b]



[a]Conditions: Substrate (**1ba**: 235 mg, 1 mmol) and RMgBr (1.0 equiv.) in THF (3 mL) at -30 °C for 30 min. [b]Isolated yield. [c]Benzyl magnesium chloride was used.

Having studied the scope of aryl amides, transformation of different alkyl amides into aryl ketones was investigated with phenyl and *p*-tolylmagnesium bromides (Scheme 8). To our delight, *N*-Boc protected *N*-methylphenylacetamide (**1ga**), *N*-benzylhexanamide (**1ha**) and *N*-methyloctanamide (**1ia**) were efficiently converted into corresponding aryl-alkyl ketones (**3ae**, **3ag-3ak**) in 67-75% yields under optimized condition.

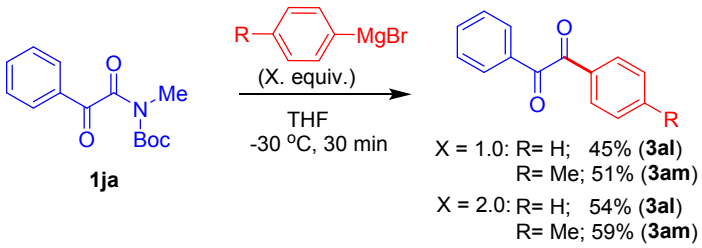
Scheme 8. Synthesis of aryl ketones: Scope of alkyl amides. [a,b]



[a]Conditions: Substrate (1 mmol) and R^3MgBr (1.0 equiv.) in THF (3 mL) at -30 °C for 30 min. [b]Isolated yield.

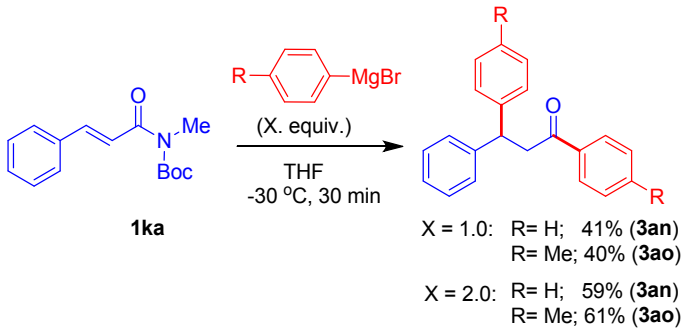
The scope of the methodology was further evaluated with sensitive group functionalized substrates such as 2-ketoamide and α,β-unsaturated amide (Scheme 9 and 10). In the case of 2-oxo-2-phenylacetamide (**1ja**), the desired diketone compounds (**3al** and **3am**) were obtained in 45-51% yields with 1.0 equiv. of Grignard reagents. There was only slight increment in yields observed with 2.0 equiv. of Grignard reagents (Scheme 9).

Scheme 9. Reaction of Grignard reagent with 2-oxo-2-Phenylacetamide.



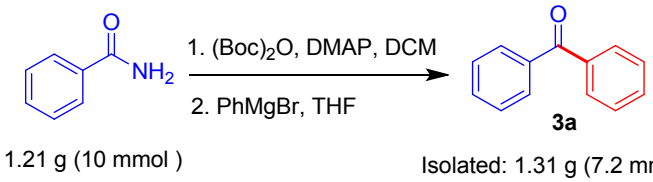
Interestingly, the *N*-Boc *N*-methyl cinnamamide (**1ka**) undergoes 1,4-addition followed by *C*(*O*)-*N* cleavage to provide diarylpropiophenones (**3an** and **3ao**) in >40% yields under optimized conditions. However, the yields of the reactions were increased subsequently (i.e. up to 61%) with the increased amount of Grignard reagents (Scheme 10).

Scheme 10. Reaction of Grignard reagent with cinnamamide.



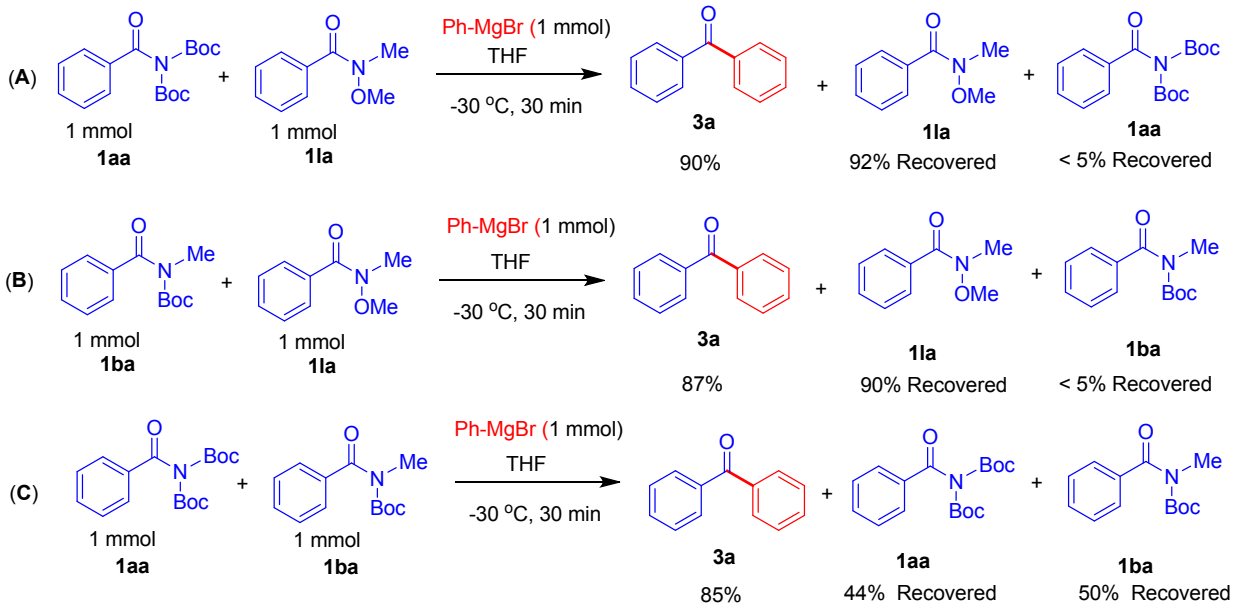
Finally, the coupling reaction was attempted in a gram scale, where 1.21 gram of benzamide was successfully converted into diphenyl ketone (**3a**) in 1.31 g over two steps (72% overall yield) which clearly demonstrates the practical applicability of the developed methodology (Scheme 11).

Scheme 11. Coupling Reaction in gram scale.



To understand the reactivity of Boc-protected amides over Weinreb amides, few competitive experiments were conducted with a controlled amount of Grignard reagents (**Scheme 12**). For instance, 1:1 mixture of *N*,*N*-di-Boc benzamide (1.0 mmol) and *N*-methoxy-*N*-methylbenzamide (1.0 mmol) was reacted with 1.0 mmol of phenyl magnesium bromide at -30 °C in THF (**Scheme 12, A**). Interestingly, *N*,*N*-di-Boc benzamide is completely consumed providing the desired diphenyl ketone in 90% yield while the Weinreb amide *i.e.* *N*-methoxy-*N*-methylbenzamide was remained unreacted (92% was recovered after the reaction).

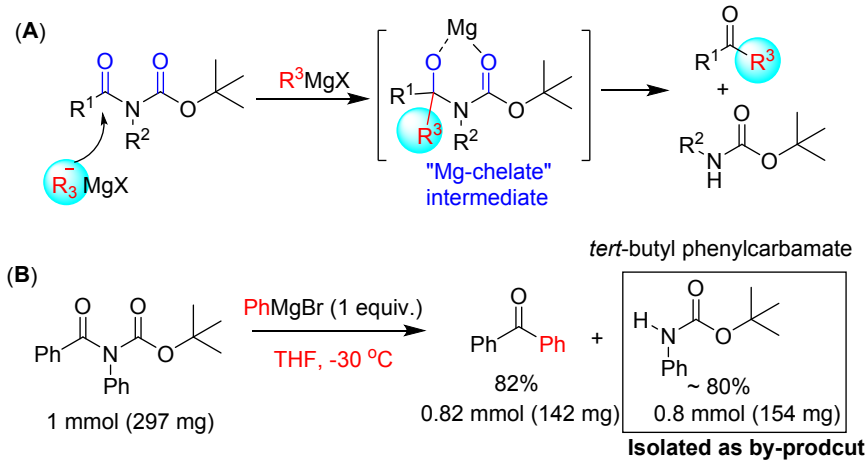
Scheme 12. Controlled experiments



Similarly, Boc protected secondary amide i.e. *N*-methyl *N*-Boc benzamide also found to be more reactive than the Weinreb amide (**Scheme 12, B**). On the other hand, it was observed that the Boc-protected primary amide (**1aa**) and secondary amide (**1ab**) showed equal reactivity with Grignard reagent (**Scheme 12, C**). For instance, almost an equal amount of Boc protected primary and secondary amides was recovered when 1.0 mmol of phenyl magnesium bromide was treated with 1:1 mixture of *N*,*N*-di-Boc benzamide (1.0 mmol) and *N*-methyl *N*-Boc benzamide (1.0 mmol). Overall, the controlled experiments suggest that Weinreb amides are less reactive when compared with Boc-protected amides in Grignard reactions while Boc-protected primary and secondary amides have equal reactivities.

A plausible mechanism for the transformation of amide to ketone is shown in Scheme 13. The nucleophile R_3 preferably attacks at the more electrophilic amide carbon and forms magnesium-chelate intermediate (**Scheme 13, A**). As seen in the Table 1 (entries 10-12), with excess amount of Grignard reagent, the coupling reaction gave the desired product approximately in same yield suggesting that the reaction might proceed through metal-chelate intermediate. This intermediate undergoes *C(O)-N* bond cleavage to yield the desired ketone and carbomate by-product. In the case of *N*-phenyl *N*-Boc benzamide (**1fa**), the carbomate byproduct was isolated and characterized (**Scheme 13, B**).

Scheme 13. (A) A plausible mechanism for the transformation of amide to ketone; (B) Evidence for the formation of the by-product.



In conclusion, a mild and practical method for the transformation of amides into ketones *via* chemoselective *C(O)-N* bond cleavage was demonstrated with Grignard reagents. A wide range of aryl and alkyl *N*-Boc protected amides underwent coupling with different aryl and alkyl Grignard reagents under catalyst-free conditions. α-Ketoamide was successfully converted into aryl diketones in the presence of Grignard reagents while unsaturated amide undergoes 1,4-addition followed by *C(O)-N* bond cleavage to provide diarylpropiophenones. Broad substrate scope, excellent functional group tolerance and quick conversion make this a very attractive methodology in organic synthesis.

Experimental Section

General information: All the solvents and chemicals were purchased from commercial sources and used without further purifications. The reactions were carried out in round bottom flask under argon atmosphere. Thin layer chromatography was performed using pre-coated plates purchased from E. Merck (*TLC silica gel 60 F254*). TLC plates were visualized by exposure to ultraviolet light (UV) with 254 nm of wavelength and then further analyzed by using iodine chamber. The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate/hexane as an eluent. The ^{1}H and ^{13}C NMR spectra were recorded on *Bruker Avance 500 MHz NMR spectrometer* using $CDCl_3$. HRMS-Mass spectra were recorded on UHD Q-Tof (ESI-TOF) using *water's Quattro Micro V 4.1* mass analyzer. In ^{1}H NMR, $CDCl_3$ peak is graduated to 7.26 ppm and it is 77.00 ppm for ^{13}C NMR spectra. The ^{1}H NMR and ^{13}C NMR of the known products were compared with literature reports. All the coupling

reactions were performed in low temperature reaction bath using Eyela PSL-1810 (Made in Japan) instrument.

Experimental procedures:

Synthesis of amides:[18] Amides **(i)-(v)** were obtained from commercial sources. Preparation of other amides was accomplished in two alternative methods namely, i) coupling of acid chlorides with amine in the presence of base (Method A) and ii) coupling of acids with amine in the presence of CDI (Method B). All these amides are well known in the literature.

Method A: Benzoyl chloride derivative (10 mmol, 1.0 equiv.) and Et_3N (3.5 mL, 25 mmol) was stirred in DCM (10 mL) to which aqueous solution of ammonia (7 mL) or aqueous solution of methylamine (40% w/w solution, 3 mL) or benzylamine (1.09 mL, 10 mmol) (or) aniline (0.93 mL, 10 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 1 h at room temperature. The crude reaction mixture was washed with water and extracted with DCM. The organic layer dried over Na_2SO_4 and the solvent was removed in vacuo to obtain the desired amides in good yields (>75% yield). Using the above procedure, Benzamide, 4-Methoxybenzamide, *N*-Nitrobenzamide, 2-Fluorobenzamide, *N*-Methylbenzamide, *N*-Benzylbenzamide, *N*-Phenylbenzamide, 4-Methoxy-*N*-methylbenzamide, 4-Nitro-*N*-methylbenzamide, 2-Fluoro-*N*-methylbenzamide, *N*-methyloctanamide and *N*,*N*-diethyl benzamide were synthesized.

Method B: Benzoic acid/heterocyclic acid derivative (10 mmol, 1.0 equiv) and 1,1'-carbonyl diimidazole (CDI) (1.62 g, 10 mmol) was stirred in DCM (20 mL) for 20 min at room temperature. After that, aqueous solution of ammonia (7 mL) or aqueous solution of methylamine (40% w/w solution, 3 mL) (or) benzylamine (1.09 mL, 10 mmol) was added to the reaction mixture and allowed to stir for 3 hours at room temperature. After completion, the reaction mixture was quenched by 1N HCl (20 mL), and extracted by DCM (40 mL). The organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to afford the desired products in >70% yields. Using the above procedure, 4-Me-Benzamide, 4-OEt-Benzamide, 4-CN-Benzamide, 4-CF_3-Benzamide, 4-I-Benzamide, 4-F-Benzamide, 4-Cl-Benzamide, 4-t-Bu-Benzamide, 3-Cl-Benzamide, 3-Br-Benzamide, 3-I-Benzamide, 3-NO_2-Benzamide, 3-CF_3-Benzamide, 3,5 di-Me-Benzamide, 3-Cl,5-NO_2-Benzamide, 3,4,5 tri-OMe-

Benzamide, 2-Br-benzamide, 2-Furanamide, 3-Thiophenamide, 3-pyridinamide, 4-Me-N-methylbenzamide, 4-OEt-*N*-methylbenzamide, 4-CN-*N*-methylbenzamide,4-CF_3-*N*-methylbenzamide, 4-I-*N*-methylbenzamide, 4-F-*N*-methylbenzamide, 4-Cl-*N*-methylbenzamide, 4-t-Bu-*N*-methylbenzamide, 3-Cl-*N*-methylbenzamide, 3-Br-*N*-methylbenzamide, 3-I-*N*-methylbenzamide, 3-NO_2-*N*-methylbenzamide, 3-CF_3-N-methylbenzamide, 3,5 di-Me-*N*-methylbenzamide, 3-Cl,5-NO_2-*N*-methylbenzamide, 3,4,5 tri-OMe-N-methylbenzamide, 2-Br-N-methylbenzamide, 2-Furan-N-methylamide, 3-Thiophene-*N*-methylamide, 3-pyridine-*N*-methylamide, *N*-benzylhexanamide, *N*-methyl-2-phenylacetamide, *N*-methyl-2-oxo-2-phenylacetamide and *N*-methylcinnamamide were prepared.

Synthesis of *N*-methyl-*N*-nitrosobenzamide (vi)[16a]: *N*-Methylbenzamide (135 mg, 1 mmol) was stirred in dichloromethane (3 mL) approximately for 2 min at room temperature to which *tert*-butyl nitrite (0.179 mL, 1.5 mmol) was added *via* syringe and allowed to stir for 1 h at room temperature. After completion, dichloromethane was evaporated and then, subjected to silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding *N*-methyl *N*-nitrosobenzamide (**vi**). The product was obtained as a yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.72; Yield 82% (134 mg).[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.78 (dd, J = 8.4, 1.3 Hz, 2H), 7.61–7.57 (m, 1H), 7.48 (dd, J = 10.9, 4.6 Hz, 2H), 3.31 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ= 172.9, 132.7, 132.5, 130.7, 128.1, 26.8.

Synthesis of benzyl benzoyl(methyl)carbamate (vii): *N*-Methylbenzamide (135 mg, 1 mmol) was dissolved in THF (5 mL) to which lithium bis(trimethylsilyl)amide (LiHMDS) (1.5 mL, 1.5 mmol) was added *via* syringe at 0 °C and allowed to stir for 15 min. After that, benzyl chloroformate (Cbz-Cl) (0.285 mL, 2 mmol) was added slowly to the reaction mixture and allowed to stir at room temperature for 3 h. After completion, the reaction mixture was quenched by 1 M HCl solution (5 mL). The resulting mixture was diluted with EtOAc (60 mL) and washed with H_2O (1 × 20 mL), brine (1 × 20 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding *N*-methyl *N*-Cbz-benzamide (**vii**). The product was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.67; Yield 90% (242 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56–7.51 (m, 2H), 7.49–7.45 (m, 1H),

7.40–7.34 (m, 2H), 7.32–7.25 (m, 3H), 7.02 (dd, J = 7.7, 1.2 Hz, 2H), 5.05 (s, 2H), 3.40 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 173.0, 154.8, 136.6, 134.4, 131.2, 128.3, 128.1, 128.0, 127.5, 68.5, 32.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO_3$: 270.1130, Found 270.1116.

Synthesis of 2,2,2-trichloroethyl benzoyl(methyl)carbamate (viii): *N*-Methylbenzamide (135 mg, 1 mmol) was dissolved in THF (5 mL) to which lithium bis(trimethylsilyl)amide (LiHMDS) (1.5 mL, 1.5 mmol) was added *via* syringe at 0 °C and allowed to stir for 15 min. After that, 2,2,2-trichloroethoxycarbonyl chloride (Troc-Cl) (0.280 mL, 2 mmol) was added slowly to the reaction mixture and allowed to stir at room temperature for 3 h. After completion, the reaction mixture was quenched by 1 M HCl solution (5 mL). The resulting mixture was diluted with EtOAc (60 mL) and washed with H_2O (1 × 20 mL), brine (1 × 20 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding *N*-methyl *N*-Troc-benzamide (**viii**). The product was obtained as a yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.65; Yield 80% (248 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.59 (dd, J = 8.1, 1.0 Hz, 2H), 7.46 (dd, J = 11.7, 4.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 4.66 (s, 2H), 3.41 (s, 3H). $^{13}C\{^1H\}$ NMR(125 MHz, $CDCl_3$) δ = 172.5, 153.1, 135.7, 131.5, 127.9, 127.6, 93.8, 75.3, 32.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}Cl_3NO_3$: 309.9805, Found 309.9797.

Synthesis of phenyl benzoyl(methyl)carbamate (ix): *N*-Methylbenzamide (135 mg, 1 mmol) was dissolved in THF (5 mL) to which lithium bis(trimethylsilyl)amide (LiHMDS) (1.5 mL, 1.5 mmol) was added *via* syringe at 0 °C and allowed to stir for 15 min. After that, phenyl chloroformate (PhOCOCl) (0.251 mL, 2 mmol) was added slowly to the reaction mixture and allowed to stir at room temperature for 3 h. After completion, the reaction mixture was quenched by 1 M HCl solution (5 mL). The resulting mixture was diluted with EtOAc (60 mL) and washed with H_2O (1 × 20 mL) and brine (1 × 20 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding phenyl benzoyl(methyl)carbamate (**ix**). The product was obtained as a white solid. M.p. 79-81 °C. The residue was purified by column chromatography in silica gel eluting with hexane:

EtOAc (90:10), R_f = 0.64; Yield 81% (206 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71–7.64 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 2H), 3.50 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 173.0, 153.3, 150.1, 136.5, 131.6, 129.3, 128.2, 127.7, 126.0, 120.7, 33.3**.** HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{15}H_{14}NO_3$: 256.0974, Found 256.0963.

Synthesis of 3-benzoyloxazolidin-2-one (x)[19]: Oxazolidinone (0.87 g, 10 mmol) and Et_3N (2.78 mL, 20 mmol) was stirred in DCM (20 mL) to which benzoyl chloride (1.16 mL, 10 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 4 h at room temperature. The crude reaction mixture was diluted with water and extracted with DCM. The organic layer dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding 3-benzoyloxazolidin-2-one (**x**). The product was obtained as a white solid. M.p. 141-143 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.55; Yield 75% (1.44 g).[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.57–7.50 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.46 (t, *J* = 7.8 Hz, 2H), 4.15 (t, *J* = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 169.7, 153.1, 132.5, 132.3, 129.0, 127.8, 62.2, 43.6.

Synthesis of 3-benzoylbenzo[d]oxazol-2(3H)-one (xi)[20]: Benzo[d]oxazol-2(3H)-one (0.540 g, 4 mmol) and Et_3N (1.114 mL, 8 mmol) was stirred in DCM (10 mL) to which benzoyl chloride (0.556 mL, 4.8 mmol) was added dropwise at 0 °C. The resulting mixture was refluxed for 2 h. The crude reaction mixture was diluted with water and extracted with EtOAc. The organic layer dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding 3-Benzoylbenzo[d]oxazol-2(3H)-one (**xi**). The product was obtained as a white solid. M.p. 182-185 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), Rf = 0.59; Yield 72% (0.688 g).[20] ^{1}H NMR (500 MHz, CDCl3) δ = 7.88–7.84 (m, 1H), 7.83–7.79 (m, 2H), 7.67–7.62 (m, 1H), 7.52 (dd, J = 11.1, 4.6 Hz, 2H), 7.31–7.26 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, CDCl3) δ = 167.7, 150.9, 142.6, 133.5, 132.0, 129.5, 128.3, 125.2, 124.6, 114.9, 110.1.

General procedure for the synthesis of *N,N*-di-Boc benzamides: The *N,N*-di-Boc benzamides were prepared using the general literature prodcure**.[9a]** Primary amide (1 mmol, 1.0 equiv.), DMAP (13 mg, 0.1 mmol.) was dissolved in dichloromethane (5 mL) and placed under a positive

pressure of argon. Di-*tert*-butyl dicarbonate (Boc_2O) (0.45 mL, ~2.1 mmol) was added to the reaction mixture with vigorous stirring at 0 °C. The resulting reaction mixture was continued to stir for 12-15 h at room temperature. After completion, the reaction mixture was quenched with saturated solution of $NaHCO_3$ (10 mL) followed by extracted with EtOAc (3 × 20 mL). The organic layer was washed with H_2O (1 × 20 mL), brine (1 × 20 mL), dried and concentrated. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding *N,N*-di-Boc benzamide (**1aa**-**1au**).

***N,N*-Boc$_2$-benzamide (1aa)**[9a]**:** The title compound was obtained as a white solid. M.p. 58-60 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.57; Yield 85% (272 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (t, J = 8.8 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 1.34 (d, J = 10.9 Hz, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 169.1, 149.6, 134.0, 133.3, 128.9, 128.5, 84.1, 27.4.

***N,N*-Boc$_2$-4-methylbenzamide (1ab)**[9a]: The title compound was obtained as a white solid. M.p. 65-67 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.59; Yield 79% (265 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 169.0, 149.8, 144.5, 131.3, 129.3, 129.3, 84.0, 27.6, 21.7.

***N,N*-Boc$_2$-4-methoxybenzamide (1ac)**[9a]: The title compound was obtained as a white solid. M.p. 71-73 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.35; Yield 62% (217 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, CDCl3) δ = 168.1, 163.9, 149.7, 131.6, 126.3, 113.9, 83.8, 55.4, 27.5.

***N,N*-Boc$_2$-4-ethoxybenzamide (1ad)**: The title compound was obtained as a white solid. M.p. 114-116 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.32; Yield 65% (237 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.08 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 168.1, 163.4, 149.7, 131.6, 126.0, 114.3, 83.7, 63.8, 27.5, 14.5. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{19}H_{28}NO_6$: 366.1917, Found 366.1900.

***N,N*-Boc$_2$-4-(trifluoromethyl)benzamide (1ae)**[9a]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with

hexane: EtOAc (90:10), R_f = 0.43; Yield 72% (281 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.90 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 1.40 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ= 168.3, 149.5, 137.5, 134.56 (q, J= 33.75 Hz), 129.1, 125.65 (q, J= 3.75 Hz), 125.58 (q, J= 271.25 Hz), 84.9, 27.5.

***N,N*-Boc$_2$-4-nitrobenzamide (1af)**[8c]: The title compound was obtained as a yellow solid. M.p. 63-65 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.41; Yield 84% (307 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.30 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H), 1.42 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 167.8, 150.1, 149.3, 139.6, 129.5, 123.7, 85.2, 27.5.

***N,N*-Boc$_2$-4-iodobenzamide (1ag)**[8f]: The title compound was obtained as a white solid. M.p. 114-117 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.52; Yield 88% (393 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.83 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 1.39 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 168.78, 149.5, 137.9, 133.5, 130.3, 101.1, 84.5, 27.5.

***N,N*-Boc$_2$-4-chlorobenzamide (1ah)**[9a]: The title compound was obtained as a white solid. M.p. 58-61 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.51; Yield 70% (249 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.76 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 1.39 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 168.3, 149.5, 139.8, 132.5, 130.4, 129.0, 84.5, 27.5.

***N,N*-Boc$_2$-4-fluorobenzamide (1ai)**[9a]: The title compound was obtained as a white solid. M.p. 67-68 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.50; Yield 73% (247 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88–7.80 (m, 2H), 7.13 (td, J = 8.4, 3.4 Hz, 2H), 1.37 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 168.0, 165.84 (d, J = 255 Hz), 149.6, 131.71 (d, J = 8.75 Hz), 130.38 (d, J = 2.5 Hz), 115.91 (d, J = 22.5 Hz), 84.3, 27.5.

***N,N*-Boc$_2$-4-tert-butylbenzamide (1aj)**: The title compound was obtained as a white solid. M.p. 68-70 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.60; Yield 72% (271 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 1.36 (s, 18H), 1.33 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 169.0, 157.4, 149.9, 131.4, 129.1, 125.6, 84.0, 35.1, 31.0, 27.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{21}H_{31}NNaO_5$: 400.2100, Found 400.2090

***N,N*-Boc$_2$-3-chlorobenzamide (1ak)**[9a]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.51; Yield 71% (252 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (t, J = 1.8 Hz, 1H), 7.70–7.67 (m, 1H), 7.55 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 1.39 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 168.1, 149.5, 135.9, 134.8, 133.1, 129.9, 128.8, 126.9, 84.6, 27.5.

***N,N*-Boc$_2$-3-bromobenzamide (1al):** The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.53; Yield 69% (276 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (t, J = 1.8 Hz, 1H), 7.77–7.66 (m, 2H), 7.34 (t, J = 7.9 Hz, 1H), 1.39 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 167.9, 149.5, 136.10, 131.7, 130.1, 127.4, 122.6, 84.7, 27.5. HRMS (ESI-TOF) m/z: [M+ Na]$^+$: Calcd for $C_{17}H_{22}BrNNaO_5$: 422.0579, Found 422.0562.

***N,N*-Boc$_2$-3-iodobenzamide (1am)**[8f]: The title compound was obtained as a yellow solid. M.p. 68-70 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.56; Yield 80% (358 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 (t, J = 1.6 Hz, 1H), 7.90 (ddd, J = 7.9, 1.6, 1.1 Hz, 1H), 7.76 (ddd, J = 7.8, 1.6, 1.1 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 1.39 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 167.8, 149.6, 142.0, 137.6, 136.1, 130.3, 128.0, 93.8, 84.7, 27.6.

***N,N*-Boc$_2$-3-(trifluoromethyl)benzamide (1an)**[9a]: The title compound was obtained as a waxy liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.65; Yield 77% (300 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 168.2, 149.5, 135.1, 132.0, 131.35 (q, J = 32.5 Hz), 129.57 (q, J = 3.75 Hz), 129.3, 125.69 (q, J = 3.75 Hz), 125.59 (q, J = 271.25 Hz), 84.9, 27.5.

***N,N*-Boc$_2$-3,5-(dimethyl)benzamide (1ao)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.60; Yield 67% (234 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.43 (s, 2H), 7.21 (s, 1H), 2.34 (s, 6H), 1.37 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ= 169.4, 149.9, 138.3, 135.0, 134.0, 126.7, 84.0, 27.4, 20.9. HRMS (ESI-TOF) m/z: [M+Na]$^+$: Calcd for $C_{19}H_{27}NNaO_5$: 372.1787, Found 372.1771.

***N,N*-Boc$_2$-(trimethoxy)benzamide (1ap)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.30; Yield 52% (214 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.06 (s, 2H), 3.90 (s, 3H), 3.86 (s, 6H), 1.38 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 168.5, 153.0, 149.8, 142.8, 128.9, 106.4, 84.2, 60.9, 56.2, 27.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{20}H_{29}NNaO_8$: 434.1791, Found 434.1777.

***N,N*-Boc$_2$-2-fluorobenzamide (1aq)**[8c]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.62; Yield 70% (238 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.68 (td, J = 7.5, 1.8 Hz, 1H), 7.54–7.49 (m, 1H), 7.23 (td, J = 7.6, 1.0 Hz, 1H), 7.12–7.08 (m, 1H), 1.43 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3) δ = 165.4, 159.97 (d, J = 252.5 Hz), 149.4, 134.09 (d, J = 8.75 Hz), 130.76 (d, J = 1.25 Hz), 124.36 (d, J = 3.75 Hz), 123.08 (d, J = 12.5 Hz), 115.97 (d, J = 22.5 Hz), 84.6, 27.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{17}H_{22}FNNaO_5$: 362.1380, Found 362.1374.

***N,N*-Boc$_2$-2-bromobenzamide (1ar)**: The title compound was obtained as a white solid. M.p. 94-96 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.56; Yield 67% (268 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (dd, J = 7.9, 0.9 Hz, 1H), 7.44 (dd, J = 7.6, 1.6 Hz, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.29 (td, J = 7.7, 1.6 Hz, 1H), 1.41 (s, 18H).^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.6, 149.1, 136.9, 133.0, 131.6, 128.8, 127.1, 119.7, 84.9, 27.3. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{17}H_{23}BrNO_5$: 400.0760, Found 400.0769.

***N,N*-Boc$_2$-1-naphthamide (1as)**[21]: The title compound was obtained as a white solid. M.p. 67-69 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.58; Yield 77% (285 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ= 8.37 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.78 (dd, J = 7.1, 0.9 Hz, 1H), 7.59 (ddd, J= 8.4, 6.9, 1.3 Hz, 1H), 7.56–7.52 (m, 1H), 7.50–7.45 (m, 1H), 1.26 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 169.3, 149.9, 133.4, 132.7, 132.4, 130.5, 128.3, 127.85, 126.9, 126.6, 124.8, 124.4, 84.4, 27.3.

***N,N*-Boc$_2$-2-naphthamide (1at)**[9a]: The title compound was obtained as a white solid. M.p. 69-71 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.57; Yield 90% (334 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.37 (d, J = 0.8

Hz, 1H), 7.97–7.86 (m, 4H), 7.62 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.59–7.54 (m, 1H), 1.36 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 169.2, 149.8, 135.6, 132.3, 131.3, 130.6, 129.3, 128.72, 128.6, 127.8, 127.0, 124.6, 84.2, 27.5.

***N,N*-Boc$_2$-thiophene-3-carboxamide (1au)**[9a]: The title compound was obtained as a white solid. M.p. 71-73 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.49; Yield 72% (235 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 8.01–7.93 (m, 1H), 7.38 (ddd, J = 10.0, 3.8, 2.4 Hz, 1H), 7.31 (dd, J = 4.2, 2.4 Hz, 1H), 1.34 (s, 18H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 163.0, 149.4, 137.3, 133.2, 127.3, 126.6, 83.9, 27.4.

General procedure for the synthesis of *N*-Boc amides: The *N*-Boc benzamides were prepared using the literature prodcure.[17d] An oven-dried round-bottomed flask (100 mL) was charged with a secondary amide (5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.5 mmol) was dissolved in dichloromethane (10 mL). Di-*tert*-butyl dicarbonate (Boc_2O) (1.5 mL, 6.5 mmol.) was added in one portion and the reaction mixture was allowed to stir for 10-12 h at room temperature. After completion, the reaction mixture was quenched with saturated solution of $NaHCO_3$ (10 mL) followed by extracted with EtOAc (3 × 20 mL). The organic layer was washed with H_2O (1 × 20 mL), brine (1 × 20 mL), dried and concentrated. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane) to obtain the corresponding *N*-Boc benzamide (**1ba-1bz**).

***tert*-Butyl benzoyl(methyl)carbamate (1ba)**[17d]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.55; Yield 80% (188 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.47 (dd, J = 8.0, 1.0 Hz, 2H), 7.44–7.40 (m, 1H), 7.35 (dd, J = 10.6, 4.3 Hz, 2H), 3.27 (s, 3H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 173.4, 153.3, 137.8, 130.7, 127.8, 127.2, 82.8, 32.3, 27.2.

***tert*-Butyl benzoyl(isopropyl)carbamate (1ca)**[22]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.55; Yield 74% (194 mg).^1H NMR (500 MHz, $CDCl_3$) δ= 7.54 (dd, J = 8.0, 1.0 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 4.72–4.63 (m, 1H), 1.42 (d, J = 6.9 Hz, 6H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 173.4, 153.3, 138.6, 131.0, 128.1, 127.4, 82.4, 48.8, 27.3, 20.3.

***tert*-Butyl benzoyl(cyclopropyl)carbamate (1da)**: The title compound was obtained as a white solid. M.p. 78-81 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.54; Yield 76% (200 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = δ = 7.56–7.51 (m, 2H), 7.50–7.44 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 2.88–2.82 (m, 1H), 1.17 (s, 9H), 1.0–0.97 (m, 2H), 0.76–0.71 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 174.7, 153.6, 137.6, 131.6, 128.0, 127.8, 82.6, 28.1, 27.4, 8.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{15}H_{19}NaNO_3$: 284.1263, Found 284.1247.

***tert*-Butyl benzoyl(benzyl)carbamate (1ea)**[17d]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.58; Yield 71% (220 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (dd, J = 7.9, 0.8 Hz, 2H), 7.47–7.42 (m, 3H), 7.40–7.29 (m, 5H), 4.99 (s, 2H), 1.12 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 173.1, 153.4, 137.78, 137.6, 131.0, 128.4, 128.1, 128.0, 127.4, 127.3, 83.1, 48.8, 27.3.

***tert*-Butyl benzoyl(phenyl)carbamate (1fa)**[17d]: The title compound was obtained as a white solid. M.p. 99-102 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.57; Yield 73% (217 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78–7.73 (m, 2H), 7.57–7.52 (m, 1H), 7.49–7.42 (m, 4H), 7.39–7.33 (m, 1H), 7.31–7.28 (m, 2H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 172.7, 153.2, 139.0, 136.9, 131.6, 129.1, 128.2, 128.0, 127.9, 127.7, 83.4, 27.4.

***tert*-Butyl methyl(4-methylbenzoyl)carbamate (1bb)**[23]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.56; Yield 82% (204 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 3.23 (s, 3H), 2.32 (s, 3H), 1.12 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ = 173.3, 153.3, 141.1, 134.5, 128.3, 127.4, 82.4, 32.3, 27.1, 21.2.

***tert*-Butyl (4-methoxybenzoyl)(methyl)carbamate (1bc)**[17d]: The title compound was obtained as a white solid. M.p. 68-71°C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.35; Yield 78% (206 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 3.27 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 173.2, 162.0, 153.8, 129.9, 129.7, 113.1, 82.6, 55.4, 32.8, 27.5.

***tert*-Butyl (4-ethoxybenzoyl)(methyl)carbamate (1bd):** The title compound was obtained as a white solid. M.p. 94-96 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.38; Yield 75% (209 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.54–7.49 (m, 2H), 6.90–6.86 (m, 2H), 4.08 (q, J = 7.0 Hz, 2H), 3.29 (s, 3H), 1.23 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 173.2, 161.4, 153.8, 129.9, 129.5, 113.6, 82.5, 63.6, 32.7, 27.4, 14.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{15}H_{21}NNaO_4$: 302.1368, Found 302.1370.

***tert*-Butyl methyl(4-(trifluoromethyl)benzoyl)carbamate (1be)**[17d]: The title compound was obtained as a white solid. M.p. 61-64. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.65; Yield 77% (233 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.66 (d, J = 8.5 Hz, 2H), 7.62–7.55 (m, 2H), 3.32 (d, J = 0.9 Hz, 3H), 1.17 (d, J = 0.9 Hz, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 172.0, 152.9, 141.3, 132.34 (q, J = 32.5 Hz), 127.4, 125.03 (q, J = 3.75 Hz), 123.66 (q, J = 270 Hz), 83.6, 32.4, 27.3.

***tert*-Butyl methyl(4-nitrobenzoyl)carbamate (1bf)**: The title compound was obtained as a pale yellow solid. M.p. 148-149 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.41; Yield 72% (202 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.31–8.25 (m, 2H), 7.67–7.61 (m, 2H), 3.35 (s, 3H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 171.2, 152.6, 148.6, 143.7, 127.8, 123.3, 84.1, 32.3, 27.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{16}N_2NaO_5$: 303.0957, Found 303.0946.

***tert*-Butyl (4-iodobenzoyl)(methyl)carbamate (1bg)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.59; Yield 67% (242 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74–7.69 (m, 2H), 7.23–7.18 (m, 2H), 3.26 (s, 3H), 1.18 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 172.5, 153.1, 137.1, 137.0, 128.9, 97.2, 83.2, 32.4, 27.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{16}INNaO_3$: 384.0073, Found 384.0065.

***tert*-Butyl (4-chlorobenzoyl)(methyl)carbamate (1bh):** The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.57; Yield 74% (199 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 (s, 2H), 7.37 (s, 2H), 3.28 (s, 3H), 1.20 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 172.4, 153.2, 136.9, 136.0, 128.8, 128.1, 83.2, 32.5, 27.4. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{13}H_{17}ClNO_3$: 270.0897, Found 270.0894.

***tert*-Butyl (4-fluorobenzoyl)(methyl)carbamate (1bi)**[23]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.56; Yield 77% (195 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56–7.48 (m, 2H), 7.10–7.03 (m, 2H), 3.28 (s, 3H), 1.19 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 172.4, 164.25 (d, J = 250 Hz), 153.3, 133.77 (d, J = 3.75 Hz), 129.82 (d, J = 8.75 Hz), 115.01 (d, J = 21.25 Hz), 83.1, 32.6, 27.4.

***tert*-Butyl (4-(tert-butyl)benzoyl)(methyl)carbamate (1bj):** The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.61; Yield 74% (215 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.44 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 3.28 (s, 3H), 1.31 (s, 9H), 1.13 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 173.5, 154.4, 153.6, 134.9, 127.3, 124.8, 82.6, 34.8, 32.5, 31.1, 27.2. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{17}H_{26}NO_3$: 292.1913, Found 292.1907.

***tert*-Butyl (3-chlorobenzoyl)(methyl)carbamate (1bk)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.56; Yield 71% (191 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.41 (d, J = 1.6 Hz, 1H), 7.39–7.32 (m, 2H), 7.31–7.24 (m, 1H), 3.24 (s, 3H), 1.13 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 171.5, 152.8, 139.2, 133.6, 130.4, 129.2, 127.2, 125.2, 83.1, 32.2, 27.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{16}ClNNaO_3$: 292.0716, Found 292.0723.

***tert*-Butyl (3-bromobenzoyl)(methyl)carbamate (1bl)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.57; Yield 70% (219 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.60–7.47 (m, 2H), 7.44 – 7.34 (m, 1H), 7.26–7.16 (m, 1H), 3.24 (s, 3H), 1.13 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 171.5, 152.9, 139.5, 133.4, 130.1, 129.5, 125.7, 121.7, 83.2, 32.3, 27.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{16}NaBrNO_3$: 336.0211, Found 336.0199.

***tert*-Butyl (3-iodobenzoyl)(methyl)carbamate (1am)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.58; Yield 72% (260 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.79–7.73 (m, 2H), 7.47–7.43 (m, 1H), 7.11 (dd, J = 11.8, 4.1 Hz, 1H), 3.26 (s, 3H), 1.16 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 171.4, 152.9, 139.6, 139.3, 135.8, 129.7, 126.3, 93.0, 83.3, 32.3, 27.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{15}H_{21}NNaO_4$: 302.1368, Found 302.1370.

***tert*-Butyl methyl(3-(trifluoromethyl)benzoyl)carbamate (1bn)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.63; Yield 76% (230 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77–7.63 (m, 3H), 7.50 (t, J = 7.8 Hz, 1H), 3.28 (s, 3H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 171.8, 152.8, 138.6, 130.4, 130.38 (d, J = 32.5 Hz), 128.6, 127.06 (q, J = 3.75 Hz), 124.09 (q, J = 3.75 Hz), 123.58 (q, J = 270 Hz), 83.4, 32.3, 27.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{14}H_{16}NaF_3NO_3$: 326.0980, Found 326.0972.

***tert*-butyl (3,5-dimethylbenzoyl)(methyl)carbamate (1bo)**[23]: The title compound was obtained as a white solid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.60; Yield 84% (220 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.12–7.09 (m, 2H), 7.08 (s, 1H), 3.28 (s, 3H), 2.31 (s, 6H), 1.15 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 173.8, 153.7, 137.6, 137.5, 132.3, 125.1, 82.6, 32.4, 27.3, 21.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{15}H_{21}NNaO_3$: 286.1419, Found 286.1415.

***tert*-Butyl methyl(3,4,5-trimethoxybenzoyl)carbamate (1bp)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.35; Yield 60% (195 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.75 (s, 2H), 3.86 (s, 3H), 3.85 (s, 6H), 3.28 (s, 3H), 1.21 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 173.1, 153.6, 152.8, 140.6, 132.9, 105.0, 82.8, 60.9, 56.1, 32.7, 27.4. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{16}H_{24}NO_6$: 326.1604, Found 326.1622.

***tert*-Butyl (2-fluorobenzoyl)(methyl)carbamate (1bq)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.58; Yield 76% (192 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48 (td, J = 7.4, 1.8 Hz, 1H), 7.43–7.39 (m, 1H), 7.19 (td, J = 7.6, 1.0 Hz, 1H), 7.07–7.01 (m, 1H), 3.33 (s, 3H), 1.21 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 168.1, 158.47 (d, J = 248.75 Hz), 152.7, 131.78 (d, J = 8.75 Hz), 129.24 (d, J = 2.5 Hz), 126.60 (d, J = 15.0 Hz), 124.19 (d, J = 3.75 Hz), 115.21 (d, J = 21.25 Hz), 83.3, 31.9, 27.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{16}FNNaO_3$: 276.1012, Found 276.1020.

***tert*-Butyl (2-bromobenzoyl)(methyl)carbamate (1br)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.55; Yield 72% (226 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.54 (dd, J = 8.0, 0.9 Hz, 1H), 7.36 (td, J = 7.5, 1.1 Hz, 1H), 7.31–7.23 (m, 2H), 3.36 (s, 3H), 1.18 (s,

9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.4, 152.1, 140.6, 132.3, 130.1, 127.5, 127.2, 118.2, 83.4, 31.3, 27.3. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{13}H_{17}BrNO_3$: 314.0392, Found 314.0391.

***tert*-Butyl (1-naphthoyl)(methyl)carbamate (1bs)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.61; Yield 65% (185 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 (dt, J = 9.4, 4.7 Hz, 3H), 7.53–7.42 (m, 4H), 3.46 (s, 3H), 0.75 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 172.4, 152.9, 136.7, 133.2, 129.8, 129.5, 128.2, 126.9, 126.2, 124.7, 124.4, 123.7, 82.9, 31.7, 26.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{17}H_{19}NNaO_3$: 308.1263, Found 308.1261.

***tert*-Butyl (2-naphthoyl)(methyl)carbamate (1bt)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.60; Yield 68% (194 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.85 (t, J = 8.4 Hz, 3H), 7.59 (d, J = 8.5 Hz, 1H), 7.55–7.48 (m, 2H), 3.37 (s, 3H), 1.06 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 173.5, 153.5, 134.8, 134.2, 132.2, 128.5, 127.6, 127.5, 127.4, 126.6, 124.3, 82.8, 32.5, 27.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calc. for $C_{17}H_{19}NNaO_3$: 308.1263, Found 308.1262.

***tert*-Butyl methyl(thiophene-3-carbonyl)carbamate (1bu)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.51; Yield 68% (164 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.70–7.66 (m, 1H), 7.25–7.22 (m, 1H), 7.18 (dd, J = 5.0, 1.1 Hz, 1H), 3.23 (s, 3H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 168.0, 153.4, 138.8, 128.8, 127.1, 124.9, 82.7, 32.5, 27.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{11}H_{15}NNaO_3S$: 264.0670, Found 264.0676.

***tert*-Butyl (4-cyanobenzoyl)(methyl)carbamate (1bv)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.45; Yield 73% (190 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71–7.67 (m, 2H), 7.57–7.53 (m, 2H), 3.30 (s, 3H), 1.19 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 171.4, 152.6, 141.9, 131.8, 127.5, 118.0, 113.9, 83.9, 32.3, 27.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{14}H_{16}NaN_2O_3$: 283.1059, Found 283.1049.

***tert*-Butyl methyl(3-nitrobenzoyl)carbamate (1bw)**: The title compound was obtained as a white solid. M.p. 91-93 °C. The residue was purified by column chromatography in silica gel

eluting with hexane: EtOAc (95:05), R_f = 0.36; Yield 68% (190 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.32 (d, J = 7.9 Hz, 2H), 7.83 (dd, J = 7.4, 0.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 3.33 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 170.8, 152.7, 147.6, 139.2, 133.0, 129.1, 125.1, 122.4, 83.9, 32.5, 27.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{16}N_2NaO_5$: 303.0957, Found 303.0962.

***tert*-Butyl (3-chloro-5-nitrobenzyl)(methyl)carbamate (1bx)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.30; Yield 65% (204 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (d, J = 2.0 Hz, 1H), 7.65 (dd, J = 8.3, 2.0 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 3.30 (s, 3H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 169.9, 152.6, 147.2, 137.2, 131.6, 131.5, 129.1, 124.5, 84.2, 32.5, 27.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{13}H_{15}ClN_2NaO_5$: 337.0567, Found 337.0561.

***tert*-Butyl (furan-2-carbonyl)(methyl)carbamate (1by)**[17d]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.52; Yield 69% (155 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 (dd, J = 1.7, 0.8 Hz, 1H), 7.04 (dd, J = 3.5, 0.8 Hz, 1H), 6.51–6.47 (m, 1H), 3.22 (s, 3H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 162.62, 153.2, 148.7, 143.9, 116.3, 111.9, 82.7, 32.3, 27.5.

***tert*-Butyl methyl(nicotinoyl)carbamate (1bz)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.37; Yield 57% (135 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.64 (dd, J = 3.6, 2.2 Hz, 2H), 7.31–7.23 (m, 2H), 3.26 (s, 3H), 1.14 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 170.9, 152.3, 149.6, 145.4, 136.8, 130.0, 120.5, 84.0, 31.9, 27.1. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{12}H_{17}N_2O_3$: 237.1239, Found 237.1235.

***tert*-Butyl methyl(2-phenylacetyl)carbamate (1ga)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.52; Yield 54% (134 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (dd, J = 9.4, 5.5 Hz, 2H), 7.28–7.24 (m, 3H), 4.26 (s, 2H), 3.18 (s, 3H), 1.53 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 174.2, 153.2, 135.1, 129.5, 128.2, 126.6, 83.0, 44.3, 31.7, 27.9. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{14}H_{20}NO_3$: 250.1443, Found 250.1444.

***tert*-Butyl benzyl(hexanoyl)carbamate (1ha)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.51; Yield 67% (204 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32–7.25 (m, 5H), 4.91 (s, 2H), 2.95–2.89 (m, 2H), 1.70 (dd, J = 14.9, 7.5 Hz, 2H), 1.43 (s, 9H), 1.35 (dq, J = 5.9, 3.9 Hz, 4H), 0.92 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 176.2, 153.1, 138.3, 128.2, 127.4, 126.9, 82.9, 47.2, 38.2, 31.3, 27.8, 24.8, 22.4, 13.9. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calcd for $C_{18}H_{28}NO_3$: 306.2069, Found 306.2074.

***tert*-Butyl methyl(octanoyl)carbamate (1ia)**: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.50; Yield 66% (170 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.12 (s, 3H), 2.83 (dd, J = 9.6, 5.6 Hz, 2H), 1.65–1.60 (m, 2H), 1.52 (s, 9H), 1.34–1.21 (m, 8H), 0.87 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 176.3, 153.3, 82.7, 38.3, 31.7, 31.4, 29.2, 29.1, 28.0, 25.1, 22.6, 14.0. HRMS (ESI-TOF) m/z: $[M+H]^+$: Calc. for $C_{14}H_{28}NO_3$: 258.2069, Found 258.2070.

***tert*-Butyl methyl(2-oxo-2-phenylacetyl)carbamate (1ja):** The title compound was obtained as a white solid. M.p. 72-74 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.62; Yield 64% (168 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87–7.79 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 3.29 (s, 3H), 1.26 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 187.8, 169.8, 151.7, 134.1, 132.8, 129.4, 128.7, 86.0, 29.8, 27.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{14}H_{17}NNaO_4$: 286.1055, Found 286.1062.

***tert*-Butyl cinnamoyl(methyl)carbamate (1ka):** The title compound was obtained as a white solid. M.p. 82-83 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.46; Yield 63% (164 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, J = 15.6 Hz, 1H), 7.58–7.49 (m, 3H), 7.40–7.33 (m, 3H), 3.23 (s, 3H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 168.9, 153.4, 142.9, 135.1, 129.8, 128.7, 128.0, 121.4, 83.0, 31.8, 28.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$: Calcd for $C_{15}H_{19}NNaO_3$: 284.1263, Found 284.1272.

Experimental procedure for the transformation of amides into ketones:

Procedure for the Scheme 2: Reaction of different amides with phenylmagnesium bromide: Protected and unprotected benzamide (1 mmol) was stirred in dry THF (3 mL) under argon at -0 °C to which a solution of phenylmagnesium bromide (1.0 mL, 1M Sol. in THF, 1 equiv.) was

added dropwise. The resulting reaction mixture was allowed to stir for 15 min at 0 °C. After completion, the reaction mixture was quenched by 1 M NH_4Cl solution (5 mL) and diluted with H_2O (1 × 10 mL) and extracted with EtOAc (30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give the desired products.

Procedure for the Table 1: *N,N*-Di-Boc-benzamide **1aa** (321 mg, 1 mmol) was stirred in dry THF (3 mL) or diethyl ether (3 mL) or toluene (3 mL) under argon at different temperature to which a solution of phenylmagnesium bromide (**2a**) (1M Sol. in THF, 1.0 mL, 1 equiv.) or (1.2 mL, 1M Sol. in THF, 1.2 equiv.) or (1M Sol. in THF, 1.5 mL, 1.5 equiv.) or (1M Sol. in THF, 2.0 mL, 2.0 equiv.) was added dropwise. The resulting reaction mixture was allowed to stir for 30 min. After completion, the reaction mixture was quenched by 1 M NH_4Cl solution (5 mL) and diluted with H_2O (1 × 10 mL) and extracted with EtOAc (30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give the diphenyl ketone (**3a**).

Final optimized procedure (Schemes 3-10): *N,N*-Di-Boc-benzamide or *N*-Boc *N*-alkyl/arylbenzamide (1 mmol) was stirred in dry THF (3 mL) under argon at -30 °C to which a solution of aryl/alkyl/alkynyl grignard reagent (1 equiv.) was added dropwise. The resulting reaction mixture was allowed to stir for 30 min at -30 °C. After completion, the reaction mixture was quenched by 1 M NH_4Cl solution (5 mL) and diluted with H_2O (1 × 10 mL) and extracted with EtOAc (30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give the desired products.

The details of aryl/alkyl/alkynyl grignard reagents: PhMgBr (1 M sol in THF, Aldrich), p-TolylMgBr (1 M sol in THF, Aldrich), 2-OMePhMgBr(1 M sol in 2-MeTHF, Alfa), 3-OMePhMgBr(1 M sol in 2-MeTHF, Alfa), 4-OMePhMgBr (0.5 M sol in THF, Alfa), 2-Nap-MgBr(0.25 M sol in 2-MeTHF, Alfa), 4-t-Bu-PhMgBr (0.5 M sol in 2-MeTHF, Alfa), 4-ClPhMgBr(1 M sol in THF, Alfa), 2,4,6-tri-MePhMgBr(1 M sol in 2-MeTHF, Alfa), PhenylethynylMgBr (1 M sol in THF, Aldrich), BnMgCl (2 M sol in THF, Aldrich) and MeMgBr(3 M sol in diethyl ether). 4-CNPhMgBr was prepared using literature procedure.[24]

Benzophenone (3a)[8j]: The title compound was obtained as a white solid. M.p. 46-48 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.55; Yield 93% (170 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83–7.79 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.47 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 196.7, 137.5, 132.4, 130.0, 128.2.

Phenyl(*p*-tolyl)methanone (3b)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 55-57 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.56; Yield 94% (184 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (dd, J = 8.0, 0.9 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 196.5, 143.2, 137.8, 134.8, 132.1, 130.2, 129.8, 128.9, 128.1, 21.6.

The title compound **(3b)** also obtained from Scheme 5 in 83% (162 mg); ; from Scheme 6 in 90% (177 mg); from Scheme 7 in 81% (159 mg) and its analytical data is matching with the above mentioned.

(4-Methoxyphenyl)(phenyl)methanone (3c)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 59-60 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.35; Yield 83% (176 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.85–7.80 (m, 2H), 7.75 (dd, J = 8.0, 1.0 Hz, 2H), 7.58–7.54 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.5, 163.1, 138.2, 132.5, 131.8, 130.0, 129.6, 128.1, 113.5, 55.4.

The title compound **(3c)** also obtained from Scheme 5 in 79% (167 mg) ; from Scheme 6 in 80% (170 mg); from Scheme 7 in 70% (162 mg) and its analytical data is matching with the above mentioned.

(4-Ethoxyphenyl)(phenyl)methanone (3d)[25]: The title compound was obtained as a white solid from Scheme 3. M.p. 54-47 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.38; Yield 85% (192 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.57–7.52 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.4, 162.5, 138.2, 132.4, 131.7, 129.8, 129.6, 128.0, 113.8, 63.6, 14.6.

The title compound **(3d)** also obtained from Scheme 5 in 81% (183 mg) and its analytical data is matching with the above mentioned.

Phenyl(4-(trifluoromethyl)phenyl)methanone (3e)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 117-118 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.63; Yield 79% (197 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.1 Hz, 2H), 7.83–7.78 (m, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.65–7.60 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 195.5, 140.6, 136.6, 133.66 (q, JF = 32.5 Hz), 133.0, 130.1, 130.0, 128.4, 125.31 (q, JF = 3.75 Hz), 123.63 (q, JF = 271.25 Hz).

The title compound **(3e)** also obtained from Scheme 5 in 75% (187 mg) and its analytical data is matching with the above mentioned.

(4-Nitrophenyl)(phenyl)methanone (3f)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 141-143 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.32; Yield 81% (184 mg). ^{1}H NMR (500 MHz, CDCl3) δ = 8.36–8.30 (m, 2H), 7.96–7.91 (m, 2H), 7.80 (dd, J = 8.2, 1.0 Hz, 2H), 7.65 (dd, J = 10.7, 4.2 Hz, 1H), 7.52 (dd, J = 11.6, 4.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, CDCl3) δ = 194.7, 149.7, 142.8, 136.2, 133.4, 130.6, 130.0, 128.6, 123.5.

The title compound **(3f)** also obtained from Scheme 5 in 76% (172 mg) and its analytical data is matching with the above mentioned.

(4-Iodophenyl)(phenyl)methanone (3g)[26]: The title compound was obtained as a white solid from Scheme 3. M.p. 101-103 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.58; Yield 79% (243 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.85 (d, J = 8.3 Hz, 2H), 7.79–7.74 (m, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.54–7.46 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 195.8, 137.5, 137.0, 136.8, 132.6, 131.4, 129.9, 128.3, 100.1.

The title compound **(3g)** also obtained from Scheme 5 in 71% (218 mg) and its analytical data is matching with the above mentioned.

(4-Chlorophenyl)(phenyl)methanone (3h)[26]: The title compound was obtained as a white solid from Scheme 3. M.p. 75-76 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.58; Yield 80% (173 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (dd, J = 12.3, 4.5 Hz, 4H), 7.60 (td, J = 7.4, 0.6 Hz, 1H), 7.52–7.44 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.4, 138.8, 137.1, 135.8, 132.6, 131.4, 129.9, 128.6, 128.3.

The title compound **(3h)** also obtained from Scheme 5 in 79% (171 mg) ; from Scheme 6 in 77% (167 mg); from Scheme 7 in 74% (160 mg) and its analytical data is matching with the above mentioned.

(4-Fluorophenyl)(phenyl)methanone (3i)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 45-46 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.58; Yield 81% (162 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 (dd, J = 8.4, 5.5 Hz, 2H), 7.79–7.73 (m, 2H), 7.58 (ddd, J = 7.5, 1.2, 0.6 Hz, 1H), 7.47 (dd, J = 11.5, 4.1 Hz, 2H), 7.14 (t, J = 8.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.1, 165.26 ((d, JF = 252.5 Hz), 137.3, 133.67 (d, JF = 3.0 Hz), 132.56 (d, JF = 8.75 Hz), 132.3, 129.7, 128.2, 115.3 (d, JF = 21.25 Hz).

The title compound **(3i)** also obtained from Scheme 5 in 80% (160 mg) and its analytical data is matching with the above mentioned.

(4-(tert-Butyl)phenyl)(phenyl)methanone (3j)[8e]: The title compound was obtained as white solid from Scheme 3. M.p. 130-133 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.52; Yield 86% (205 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83–7.80 (m, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.51–7.46 (m, 4H), 1.37 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 196.3, 156.1, 137.8, 134.7, 132.1, 130.0, 129.9, 128.1, 125.1, 35.03, 31.0.

The title compound **(3j)** also obtained from Scheme 5 in 83% (198 mg) ; from Scheme 6 in 76% (181 mg); from Scheme 7 in 84% (200 mg) and its analytical data is matching with the above mentioned.

(3-Chlorophenyl)(phenyl)methanone (3k)[26]: The title compound was obtained as a white solid from Scheme 3. M.p. 83-85 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.52; Yield 81% (175 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (dd, J = 5.9, 4.5 Hz, 3H), 7.66 (dd, J = 7.6, 1.1 Hz, 1H), 7.61 (dd, J = 10.6, 4.3 Hz, 1H), 7.57–7.52 (m, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.1, 139.1, 136.8, 134.4, 132.7, 132.2, 129.9, 129.8, 129.5, 128.4, 128.0.

The title compound **(3k)** also obtained from Scheme 5 in 74% (160 mg) and its analytical data is matching with the above mentioned.

(3-Bromophenyl)(phenyl)methanone (3l)[27]: The title compound was obtained as a white solid from Scheme 3. M.p. 80-82 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.54; Yield 84% (219 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (t, J = 1.8 Hz, 1H), 7.81–7.75 (m, 2H), 7.70 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.63–7.58 (m, 1H), 7.52–7.46 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 195.0, 139.3, 136.7, 135.1, 132.7, 132.6, 129.9, 129.8, 128.4, 128.3, 122.4.

The title compound **(3l)** also obtained from Scheme 5 in 78% (203 mg) and its analytical data is matching with the above mentioned.

(3-Iodophenyl)(phenyl)methanone (3m)[27]: The title compound was obtained as a white solid from Scheme 3. M.p. 45-47 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.56; Yield 78% (240 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (t, J = 1.6 Hz, 1H), 7.91–7.89 (m, 1H), 7.81–7.76 (m, 2H), 7.75–7.71 (m, 1H), 7.62–7.58 (m, 1H), 7.51–7.46 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 194.9, 141.0, 139.3, 138.4, 136.7, 132.7, 129.9, 129.8, 129.0, 128.3, 94.0.

The title compound **(3m)** also obtained from Scheme 5 in 69% (212 mg) and its analytical data is matching with the above mentioned.

Phenyl(3-(trifluoromethyl)phenyl)methanone (3n)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 52-53 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.63; Yield 86% (215 mg). ^{1}H NMR (500 MHz, CDCl3) δ = 8.07 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.80 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, CDCl3) δ = 195.1, 138.2, 136.6, 133.1, 132.9, 130.91 (q, *J*F = 32.5 Hz), 129.9, 128.9, 128.8 (q, *J*F = 3.75 Hz), 128.5, 126.64 (q, *J*F = 3.8 Hz), 123.65 (q, *J*F = 271.25 Hz).

The title compound **(3n)** also obtained from Scheme 5 in 81% (202 mg) and its analytical data is matching with the above mentioned.

(3,5-dimethylphenyl)(phenyl)methanone (3o)[13]: The title compound was obtained as a white solid from Scheme 3. M.p.70-72 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.64; Yield 79% (166 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.60–7.55 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H),

7.41 (s, 2H), 7.22 (s, 1H), 2.37 (s, 6H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 197.1, 137.8, 137.8, 137.5, 134.0, 132.1, 129.9, 128.1, 127.7, 21.1.

The title compound **(3o)** also obtained from Scheme 5 in 75% (157 mg) and its analytical data is matching with the above mentioned.

Phenyl(3,4,5-trimethoxyphenyl)methanone (3p)[28]: The title compound was obtained as a white solid from Scheme 3. M.p. 76-79 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.42; Yield 76% (207 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (dd, J = 8.1, 1.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.05 (s, 2H), 3.92 (s, 3H), 3.86 (s, 6H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.6, 152.7, 141.9, 137.6, 132.4, 132.2, 129.7, 128.1, 107.6, 60.8, 56.2.

The title compound **(3p)** also obtained from Scheme 5 in 71% (193 mg) and its analytical data is matching with the above mentioned.

(2-Fluorophenyl)(phenyl)methanone (3q)[27]: The title compound was obtained as a dirty yellow solid from Scheme 3. M.p. 81-84 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.60; Yield 69% (138 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.59–7.52 (m, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.29 (dd, J = 9.0, 6.0 Hz, 1H), 7.18 (t, J = 9.1 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 193.4, 160.02 (d, JF = 250 Hz), 137.30, 133.38, 133.03 (d, JF = 8.75 Hz), 130.70 (d, JF = 2.5 Hz), 129.7, 128.4, 126.94 (d, JF = 15Hz), 124.23 (d, JF = 3.75 Hz), 116.22 (d, JF = 22.5 Hz).

The title compound **(3q)** also obtained from Scheme 5 in 58% (116 mg) and its analytical data is matching with the above mentioned.

(2-Bromophenyl)(phenyl)methanone (3r)[29]: The title compound was obtained as a white solid from Scheme 3. M.p. 44 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.66; Yield 67% (174 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 (dd, J = 8.3, 1.2 Hz, 2H), 7.65 (dd, J = 4.3, 3.7 Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.49–7.41 (m, 3H), 7.38–7.33 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.8, 140.6, 136.0, 133.7, 133.1, 131.1, 130.2, 128.9, 128.6, 127.1, 119.5.

The title compound **(3r)** also obtained from Scheme 5 in 54% (141 mg) and its analytical data is matching with the above mentioned.

Naphthalen-1-yl(phenyl)methanone (3s)[26]: The title compound was obtained as a white solid from Scheme 3. M.p. 72-75 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.56; Yield 76% (176 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.95–7.92 (m, 1H), 7.89 (dd, J = 8.2, 1.1 Hz, 2H), 7.60 (t, J = 7.4 Hz, 2H), 7.56–7.50 (m, 3H), 7.46 (t, J = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 197.9, 138.2, 136.2, 133.6, 133.1, 131.1, 130.8, 130.3, 128.3, 128.3 127.6, 127.1, 126.3, 125.6, 124.2.

The title compound **(3s)** also obtained from Scheme 5 in 67% (155 mg) and its analytical data is matching with the above mentioned.

Naphthalen-2-yl(phenyl)methanone (3t)[8e]: The title compound was obtained as a white solid from Scheme 3. M.p. 81-83 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.50; Yield 81% (188 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.27 (s, 1H), 7.98–7.90 (m, 4H), 7.89–7.84 (m, 2H), 7.67–7.59 (m, 2H), 7.58–7.49 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 196.7, 137.8, 135.1, 134.7, 132.3, 132.1, 131.8, 130.0, 129.3, 128.2, 128.2, 127.7, 126.7, 125.7.

The title compound **(3t)** also obtained from Scheme 5 in 74% (172 mg); from Scheme 6 in 75% (174 mg); from Scheme 7 in 70% (162 mg) and its analytical data is matching with the above mentioned.

Phenyl(thiophen-3-yl)methanone (3u)[8e]: The title compound was obtained as a colourless liquid from Scheme 3. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.49; Yield 85% (160 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (dt, J = 2.4, 1.1 Hz, 1H), 7.87–7.82 (m, 2H), 7.59 (ddd, J = 14.9, 5.2, 1.1 Hz, 2H), 7.51–7.46 (m, 2H), 7.38 (ddd, J = 4.9, 2.8, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 189.9, 141.1, 138.5, 133.9, 132.2, 129.3, 128.5, 128.3, 126.1.

The title compound **(3u)** also obtained from Scheme 5 in 77% (145 mg) and its analytical data is matching with the above mentioned.

4-Benzoylbenzonitrile (3v)[27]: The title compound was obtained as a white solid from Scheme 5. M.p. 106-109 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.60; Yield 78% (161 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, J = 8.5 Hz, 2H), 7.84–7.75 (m, 4H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.0, 141.1, 136.2, 133.3, 132.1, 130.2, 130.0, 128.6, 117.9, 115.6.

The title compound **(3v)** also obtained from Scheme 6 in 73% (151 mg); from Schem 7 in 67% (139 mg) and its analytical data is matching with the above mentioned.

(3-Nitrophenyl)(phenyl)methanone (3w)[27]: The title compound was obtained as a pale yellow solid. M.p. 97 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f= .35; Yield 74% (168 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.66–8.60 (m, 1H), 8.45 (ddd, J = 8.2, 2.2, 0.9 Hz, 1H), 8.14 (dt, J = 7.7, 1.2 Hz, 1H), 7.83–7.77 (m, 2H), 7.73–7.64 (m, 2H), 7.53 (dd, J = 10.8, 4.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 194.1, 148.0, 139.0, 136.1, 135.4, 133.3, 129.9, 129.6, 128.7, 126.7, 124.6.

(3-Chloro-5-nitrophenyl)(phenyl)methanone (3x): The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:05), R_f = 0.52; Yield 73% (191 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.28 (d, J = 1.9 Hz, 1H), 7.96 (dd, J = 8.3, 2.0 Hz, 1H), 7.78 (dd, J = 8.1, 0.9 Hz, 2H), 7.72–7.63 (m, 2H), 7.54 (t, J = 7.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 193.0, 147.7, 137.0, 135.9, 133.8, 133.4, 132.1, 131.0, 129.8, 128.8, 126.8. HRMS (ESI-TOF) m/z: $[M+H]^+$**:** Calcd for $C_{13}H_9ClNO_3$: 262.0271, Found 262.0265.

Furan-3-yl(phenyl)methanone (3y)[8e]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.51; Yield 81% (139 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98–7.92 (m, 2H), 7.71–7.68 (m, 1H), 7.60–7.55 (m, 1H), 7.51–7.45 (m, 2H), 7.22 (dd, J = 3.6, 0.5 Hz, 1H), 6.58 (dd, J = 3.6, 1.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 182.5, 152.1, 147.0, 137.1, 132.5, 129.1, 128.3, 120.5, 112.1.

Phenyl(pyridin-3-yl)methanone (3z)[8e]: The title compound was obtained as oil. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.32; Yield 72% (132 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.78 (dd, J = 4.4, 1.6 Hz, 2H), 7.78 (dd, J = 8.3, 1.3 Hz, 2H), 7.64–7.59 (m, 1H), 7.55 (dd, J = 4.4, 1.7 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 195.0, 150.2, 144.2, 135.7, 133.4, 130.0, 128.5, 122.7.

(3-Methoxyphenyl)(phenyl)methanone (3aa)[8e]: The title compound was obtained as a colourless liquid from Scheme 6. The residue was purified by column chromatography in silica

gel eluting with hexane: EtOAc (80:20), R_f = 0.42; Yield 74% (157 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (dd, J = 8.3, 1.3 Hz, 2H), 7.62–7.57 (m, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.40–7.32 (m, 3H), 7.14 (ddd, J = 8.0, 2.7, 1.2 Hz, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 196.5, 159.5, 138.8, 137.5, 132.4, 130.0, 129.2, 128.2, 122.8, 118.8, 114.2, 55.4.

The title compound **(3aa)** also obtained from Scheme 7 in 71% (150 mg) and its analytical data is matching with the above mentioned.

(2-Methoxyphenyl)(phenyl)methanone (3ab)[8e]: The title compound was obtained as a colourless liquid from Scheme 6. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.44; Yield 71% (150 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84–7.79 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (ddd, J = 19.6, 12.3, 4.6 Hz, 3H), 7.36 (dd, J = 7.5, 1.6 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 3.72 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 196.4, 157.3, 137.7, 132.9, 131.8, 129.8, 129.5, 128.7, 128.1, 120.4, 111.3, 55.5.

The title compound **(3ab)** also obtained from Scheme 7 in 68% (144 mg) and its analytical data is matching with the above mentioned.

Mesityl(phenyl)methanone (3ac)[28]: The title compound was obtained as a colourless liquid from Scheme 6. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.55; Yield 78% (175 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 6.91 (s, 2H), 2.34 (s, 3H), 2.09 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 200.7, 138.4, 137.2, 136.8, 134.1, 133.5, 129.3, 128.7, 128.2, 126.8, 21.1, 19.3.

The title compound **(3ac)** also obtained from Scheme 7 in 71% (159 mg) and its analytical data is matching with the above mentioned.

Acetophenone (3ad)[12]: The title compound was obtained as a liquid from Scheme 6. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.46; Yield 43% (52 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99–7.93 (m, 2H), 7.58–7.54 (m, 1H), 7.46 (dd, J = 11.5, 4.2 Hz, 2H), 2.61 (d, J = 0.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

The title compound **(3ad)** also obtained from Scheme 7 in 35% (42 mg) and its analytical data is matching with the above mentioned.

(3-Nitrophenyl)(phenyl)methanone (3af)[12]: The title compound was obtained as a white solid. M.p. 98-99 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.56; Yield 71% (146 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.27–8.20 (m, 2H), 7.72–7.68 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.55–7.47 (m, 3H), 7.43 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 178.0, 136.9, 134.1, 133.1, 130.8, 129.6, 128.7, 128.6, 120.1, 93.1, 86.9.

1,2-diphenylethan-1-one (3ae)[26]: The title compound was obtained as a white solid from Scheme 6. M.p. 55-57 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.40; Yield 71% (139 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 (dd, J = 8.4, 1.3 Hz, 2H), 7.59–7.54 (m, 1H), 7.50–7.44 (m, 2H), 7.37–7.32 (m, 2H), 7.31–7.24 (m, 3H), 4.30 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 197.5, 136.5, 134.4, 133.1, 129.4, 128.6, 128.5, 128.5, 126.8, 45.4.

The title compound **(3u)** also obtained from Scheme 7 in 51% (100 mg); from Scheme 8 in 71% (139 mg) and its analytical data is matching with the above mentioned.

2-Phenyl-1-(p-tolyl)ethan-1-one (3ag)[30]: The title compound was obtained as a white solid. M.p. 99-102 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.46; Yield 75% (157 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.32–7.25 (m, 5H), 4.29 (s, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 197.2, 143.9, 134.7, 134.0, 129.3, 129.2, 128.7, 128.5, 126.7, 45.3, 21.6.

1-Phenylhexan-1-one (3ah)[31]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.50; Yield 68% (120 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (dt, J = 8.5, 1.6 Hz, 2H), 7.58–7.53 (m, 1H), 7.49–7.42 (m, 2H), 3.00–2.93 (m, 2H), 1.78–1.70 (m, 2H), 1.37 (tt, J = 7.2, 3.6 Hz, 4H), 0.94–0.88 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 200.6, 137.0, 132.8, 128.5, 128.0, 38.5, 31.5, 24.0, 22.5, 13.9.

1-(p-Tolyl)hexan-1-one (3ai)[31]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.52; Yield 72% (136 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.85 (dd, J = 8.1, 1.4 Hz, 2H), 7.26–7.20 (m, 2H), 2.91 (td, J = 7.5, 2.1 Hz, 2H), 2.39 (d, J = 2.2 Hz, 3H), 1.76–1.67

(m, 2H), 1.35 (dd, J = 5.0, 2.3 Hz, 4H), 0.90 (t, J = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 200.1, 143.4, 134.5, 129.1, 128.0, 38.3, 31.4, 24.0, 22.4, 21.4, 13.88.

1-Phenyloctan-1-one (3aj)[32]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.51; Yield 67% (136 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.96 (dd, J = 8.2, 1.0 Hz, 2H), 7.55 (dd, J = 10.6, 4.1 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.78–1.68 (m, 2H), 1.36–1.27 (m, 9H), 0.88 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 200.6, 137.0, 132.8, 128.5, 128.0, 38.6, 31.6, 29.3, 29.1, 24.3, 22.6, 14.0.

1-(p-Tolyl)octan-1-one (3ak)[33]: The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.52; Yield 70% (152 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.2 Hz, 2H), 7.29–7.25 (m, 2H), 2.98–2.92 (m, 2H), 2.43 (s, 3H), 1.78–1.71 (m, 2H), 1.41–1.28 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 200.3, 143.5, 134.5, 129.1, 128.1, 38.5, 31.6, 29.3, 29.1, 24.4, 22.6, 21.5, 14.0.

Benzyl (3al)[34]: The title compound was obtained as a pale yellowsolid. M.p. 95-96 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 45% (94 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.97 (dd, J = 5.0, 4.3 Hz, 4H), 7.68–7.61 (m, 2H), 7.53–7.48 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 194.5, 134.8, 132.9, 129.8, 128.9.

1-Phenyl-2-(p-tolyl)ethane-1,2-dione (3am)[34]: The title compound was obtained as a yellow sticky oil. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.62; Yield 51% (114 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.97 (dd, J = 8.3, 1.2 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.67–7.62 (m, 1H), 7.50 (dd, J = 11.6, 4.1 Hz, 2H), 7.33–7.28 (m, 2H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 194.7, 194.2, 146.2, 134.7, 133.0, 130.5, 130.0, 129.8, 129.7, 128.9, 21.9.

1,3,3-triphenylpropan-1-one (3an)[35]: The title compound was obtained as a white solid. M.p. 94-95 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.58; Yield 41% (117 mg). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.96 (dd, J = 8.2, 1.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 4.3 Hz, 8H), 7.21 (dq, J = 8.7, 4.2 Hz, 2H), 4.86 (t, J = 7.3 Hz, 1H), 3.77 (d, J = 7.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 197.9, 144.1, 137.0, 133.0, 128.5, 128.5, 128.0, 127.8, 126.3, 45.9, 44.7.

3-Phenyl-1,3-di-p-tolylpropan-1-one (3ao)[35]: The title compound was obtained as a white solid. M.p. 115-118 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 40% (125 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (d, J = 8.2 Hz, 2H), 7.24 (dd, J = 11.0, 6.5 Hz, 6H), 7.18–7.12 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 4.78 (t, J = 7.3 Hz, 1H), 3.69 (d, J = 7.3 Hz, 2H), 2.40 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 197.6, 144.4, 143.8, 141.2, 135.8, 134.5, 129.2, 129.2, 128.5, 128.1, 127, 127.6, 126.2, 45.5, 44.6, 21.62, 20.9.

Procedure for the gram scale reaction Scheme 11: Benzamide (1.21 g, 10 mmol) and 4-DMAP (122 mg, 1 mmol) were stirred in dichloromethane (50 mL) at 0 °C under argon atmosphere to which di-*tert*-butyl dicarbonate (Boc_2O) (4.37 g, 20 mmol) was added. The resulting mixture was stirred vigorously for 15 h at room temperature. After completion, the reaction mixture was quenched with saturated solution of $NaHCO_3$ (100 mL) followed by extracted with EtOAc (3 × 100 mL). The organic layer was washed with H_2O (1 × 20 mL), brine (1 × 20 mL), dried and concentrated. The crude product was purified by silica gel (60-120 mesh) column chromatography (SiO_2: ethyl acetate/hexane, 10:90) to obtain the corresponding *N,N*-di-Bocbenzamide **1aa** in 2.66 g (8.3 mmol, 83%). Further, the compound *N,N*-di-Bocbenzamide **1aa** (2.66 g) was stirred in dry THF (25 mL) under argon at -30 °C to which a solution of phenylmagnesium bromide reagent (8.3 mL, 1M Sol. in THF) was added dropwise. The resulting mixture was stirred at -30 30 °C for 30 min. and quenched by 1 M NH_4Cl solution (10 mL). The reaction mixture was diluted with H_2O (50 mL) and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (EtOAc: hexane, 5:95) to give the diphenyl ketone in 1.37 g (87% yield).

Procedure for controlled experiment (A): A mixture of *N,N*-Di-Boc benzamide **1aa** (321 mg, 1 mmol) and Weinreb amide **1la** (165 mg, 1 mmol) were stirred in dry THF (5 mL) under argon at -30 °C to which a solution of phenylmagnesium bromide (1 mL, 1 mmol, 1 M sol in THF) was added dropwise. The resulting reaction mixture was allowed to stir for 30 min at -30 °C. After completion, the reaction mixture was quenched by 1 M NH_4Cl solution (5 mL) and diluted with H_2O (1 × 10 mL) and extracted with EtOAc (30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column

chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give **3a** (163 mg, 90%), **1la** (152 mg, 92%), **1aa** (trace amount ~ 3%).

Procedure for controlled experiment (B): A mixture of *N*-Boc *N*-methylbenzamide **1ba** (235 mg, 1 mmol) and Weinreb amide **1la** (165 mg, 1 mmol) was stirred in dry THF (5 mL) under argon at -30 °C to which a solution of phenylmagnesium bromide (1 mL, 1 mmol, 1 M sol in THF) was added dropwise. The resulting reaction mixture was allowed to stir for 30 min at -30 °C. After completion, the reaction mixture was quenched by 1 M NH_4Cl solution (5 mL) and diluted with H_2O (1 × 10 mL) and extracted with EtOAc (30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give) to give **3a** (158 mg, 87%), **1la** (148 mg, 90%), **1ba** (trace amount ~ 4%).

Procedure for controlled experiment (C): A mixture of *N,N*-Di-Boc benzamide **1aa** (321 mg, 1 mmol) and *N*-Boc *N*-methylbenzamide **1ba** (235 mg, 1 mmol) were stirred in dry THF (3 mL) under argon at -30 °C to which a solution of phenylmagnesium bromide (1 mL, 1 mmol, 1M sol in THF) was added dropwise. The resulting reaction mixture was allowed to stir for 30 min at -30 °C. After completion, the reaction mixture was quenched by 1 M NH_4Cl solution (5 mL) and diluted with H_2O (1 × 10 mL) and extracted with EtOAc (30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give **3a** (154 mg, 85%), **1aa** (141 mg, 44%), **1ba** (117 mg, 50%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Copies of ^{1}H and ^{13}C NMR of **vi-xi** Boc protected amides (**1aa-1ka, 1ab-1au, 1bb-1bz**) and ketones (**3a-3z**, **3aa-3ao**) is attached

AUTHOR INFORMATION

Corresponding Author

Email: jeyakumar.chy@iitbhu.ac.in

Author Contributions

[#] P.S and S.A contributed equally to this work

Notes

The authors declare no competing financial interest

ACKNOWLEDGEMENTS

J. K. acknowledges Max-Planck Society-Germany and DST-India (DST/INT/MPG/P-09/2016) for financial support through Indo-Max Planck partner group project. J.K. acknowledges Central Instrumentation Facility Centre (CIFC)-IIT BHU for the NMR facilities. S. A. acknowledges the CSIR for Senior Research Fellowship (SRF) (09/013(0650)/2016-EMR-I). S.S. and N.M acknowledges Pondicherry University for mass analysis.

REFERENCES

(1) (a) Trost, B. M.; Fleming, I. (Ed.), *Comprehensive Organic Synthesis*, Pergamon, Oxford, 1991; (b) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, Wiley-VCH, New York, 1989; (c) March, J. *Advanced Organic Chemistry*, Wiley-VCH, New York, 1985; (d) Wong, T. Y.; Simo R.; Mitchell, P. Fenofibrate - a potential systemic treatment for diabetic retinopathy?. *Am. J. Ophthalmol.* **2012**, *154*, 6−12; (e) J. D. Sheppard, J. D. Topical bromfenac for prevention and treatment of cystoid macular edema following cataract surgery: a review. *Clin. Ophthalmol.* **2016**, *10*, 2099−2111.

(2) Olah, G. A. *Friedel−Crafts and Related Reactions*, Wiley-Interscience, New York, Vol. 1-3, 1963−1965.

(3) Bäckvall, J.-E. *Modern Oxidation Methods*, Wiley-VCH, Weinheim, 2005.

(4) (a) Greenberg, A.; Breneman, C. M.; Liebman, J. F. *The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Materials Science*, Wiley-Interscience, New York, 2000; (b) Humphrey, J. M.; Chamberlin, A. R. Chemical Synthesis of Natural Product Peptides: Coupling Methods for the Incorporation of Noncoded Amino Acids into Peptides. *Chem. Rev*. **1997**, *97*, 2243−2266.

(5) (a) Kaiser, D.; Bauer, A.; Lemmerer, M.; Maulide, N. Amide activation: an emerging tool for chemoselective synthesis. *Chem. Soc. Rev.* **2018**, *47*, 7899−7925; (b) Liu, C.; Szostak, M. Decarbonylative cross-coupling of amides. *Org. Biomol. Chem.* **2018**, *16*, 7998−8010;

(c) Bourne-Branchu, Y.; Gosmini, C.; Danoun, G. *N*-Boc-Amides in Cross-Coupling Reactions. *Chem. Eur. J.* **2019**, *25*, 2663-2674; (d) Chaudhari, M. B.; Gnanaprakasam, B. Recent Advances in the Metal-Catalyzed Activation of Amide Bonds. *Chem. Asian J.* **2019**, *14*, 76−93.

(6) (a) Li, X.; Zou, G. Acylative Suzuki coupling of amides: acyl-nitrogen activation via synergy of independently modifiable activating groups. *Chem. Commun.* **2015**, *51*, 5089−5092; (b) Huang, P. Q.; Chen, H. Ni-Catalyzed cross-coupling reactions of *N*-acylpyrrole-type amides with organoboron reagents. *Chem. Commun.* **2017**, *53*, 12584−12587.

(7) (a) Simmons, B. J.; Weires, N. A.; Dander, J. E.; Garg, N. K. Nickel-Catalyzed Alkylation of Amide Derivatives. *ACS Catal.* **2016**, *6*, 3176−3179; (b) Dander, J. E.; Garg, N. K. Breaking Amides using Nickel Catalysis. *ACS Catal.* **2017**, *7*, 1413−1423; (c) Boit, T. B.; Weires, N. A.; Kim, J.; Garg, N. K. Nickel-Catalyzed Suzuki–Miyaura Coupling of Aliphatic Amides. *ACS Catal.* **2018**, *8*, 1003−1008; (d) Weires, N. A.; Baker, E. L.; Garg, N. K. Nickel-catalysed Suzuki-Miyaura coupling of amides. *Nat. Chem.* **2016**, *8*, 75−79.

(8) (a) Shi, S.; Nolan, S. P.; Szostak, M. Well-Defined Palladium(II)–NHC Precatalysts for Cross-Coupling Reactions of Amides and Esters by Selective N–C/O–C Cleavage. *Acc. Chem. Res.* **2018**, *51*, 2589−2599 and references cited therein; (b) Meng, G.; Szostak, M. Palladium/NHC (NHC = N-Heterocyclic Carbene)-Catalyzed B-Alkyl Suzuki Cross-Coupling of Amides by Selective N–C Bond Cleavage. *Org. Lett.* **2018**, *20*, 6789−6793; (c) Meng, G. R.; Shi, S. C.; Szostak, M. Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling of Amides via Site-Selective N–C Bond Cleavage by Cooperative Catalysis. *ACS Catal.* **2016**, *6*, 7335−7339; (d) Liu, C. W.; Meng, G. R.; Liu, Y. M.; Liu, R. Z.; Lalancette, R.; Szostak, R.; Szostak, M. *N*-Acylsaccharins: Stable Electrophilic Amide-Based Acyl Transfer Reagents in Pd-Catalyzed Suzuki–Miyaura Coupling via N–C Cleavage. *Org. Lett.* **2016**, *18*, 4194−4197; (e) Lei, P.; Meng, G. R.; Ling, Y.; An, J.; Nolan, S. P.; Szostak, M. General Method for the Suzuki–Miyaura Cross-Coupling of Primary Amide-Derived Electrophiles Enabled by [Pd(NHC)(cin)Cl] at Room Temperature. *Org. Lett.* **2017**, *19*, 6510−6513; (f) Meng G. R.; Szostak, M. Site-Selective

C–H/C–N Activation by Cooperative Catalysis: Primary Amides as Arylating Reagents in Directed C–H Arylation. *ACS Catal.* **2017**, *7*, 7251−7256.

(9) (a) Shi, S.; Szostak, M. Nickel-Catalyzed Diaryl Ketone Synthesis by N–C Cleavage: Direct Negishi Cross-Coupling of Primary Amides by Site-Selective N,N-Di-Boc Activation. *Org. Lett.* **2016**, *18*, 5872−5875; (b) Shi, S.; Szostak, M. Efficient Synthesis of Diaryl Ketones by Nickel-Catalyzed Negishi Cross-Coupling of Amides by Carbon–Nitrogen Bond Cleavage at Room Temperature Accelerated by a Solvent Effect. *Chem. Eur. J.* **2016**, *22*, 10420−10424.

(10) Knappke, C. E. I.; Jacobi von Wangelin, A. 35 years of palladium-catalyzed cross-coupling with Grignard reagents: how far have we come?. *Chem. Soc. Rev.* **2011**, *40*, 4948−4962.

(11) (a) Nahm, S.; Weinreb, S. M. *N*-methoxy-N-methylamides as Effective Acylating Agents *Tetrahedron Lett.* **1981**, *22*, 3815−3818; (b) Balasubramaniam, S.; Aidhen, I. S. The Growing Synthetic Utility of the Weinreb Amide. *Synthesis,* **2008**, 3707−3738.

(12) Liu, C. W.; Achtenhagen, M.; Szostak, M. Chemoselective Ketone Synthesis by the Addition of Organometallics to N-Acylazetidines. *Org. Lett.* **2016**, *18*, 2375−2378.

(13) Chen, C. P.; Liu, P.; Luo, M. M.; Zeng, X. M. Kumada Arylation of Secondary Amides Enabled by Chromium Catalysis for Unsymmetric Ketone Synthesis under Mild Conditions. *ACS Catal.* **2018**, *8*, 5864−5868.

(14) Giovannini, A.; Savoia, D.; Umani-Ronchi, A. Organometallic ring-opening reactions of *N*-acyl and *N*-alkoxycarbonyl lactams. Synthesis of cyclic imines *J. Org. Chem*. **1989**, *54*, 228−234.

(15) Pace, V.; Holzer, W.; Olofsson, B. Increasing the Reactivity of Amides towards Organometallic Reagents: An Overview. *Adv. Synth. Catal.* **2014**, *356*, 3697−3736.

(16) (a) Sureshbabu, P.; Azeez, S.; Chaudhary, P.; Kandasamy, J. tert-Butyl nitrite promoted transamidation of secondary amides under metal and catalyst free conditions. *Org. Biomol. Chem.* **2019**, *17*, 845−850; (b) Chaudhary, P.; Gupta, S.; Muniyappan, N.; Sabiah, S.; Kandasamy, J. Regioselective Nitration of N-Alkyl Anilines using tert-Butyl Nitrite under Mild Condition. *J. Org. Chem.* **2019**, *84*, 104−119; (c) Chaudhary, P.; Korde, R.; Gupta, S.; Sureshbabu, P.; Sabiah, S.; Kandasamy, J. An Efficient Metal-Free Method for the Denitrosation of Aryl *N*-Nitrosamines at Room Temperature. *Adv. Synth.*

Catal. **2018**, *360*, 556−561; (d) Chaudhary, P.; Gupta, S.; Sureshbabu, P.; Sabiah, S.; Kandasamy, J. A metal free reduction of aryl-N-nitrosamines to the corresponding hydrazines using a sustainable reductant thiourea dioxide. *Green Chem.* **2016**, *18*, 6215−6221; (e) Chaudhary, P.; Gupta, S.; Muniyappan, N.; Sabiah, S.; Kandasamy, J. An efficient synthesis of N-nitrosamines under solvent, metal and acid free conditions using tert-butyl nitrite. *Green Chem.* **2016**, *18*, 2323−2330.

(17) (a) Baker, E. L.; Yamano, M. M.; Zhou, Y. J.; Anthony, S. M.; Garg, N. K. A two-step approach to achieve secondary amide transamidation enabled by nickel catalysis. *Nat. Commun.* **2016**, *7*, 11554; (b) Dander, J. E.; Baker, E. L.; Garg, N. K. Nickel-catalyzed transamidation of aliphatic amide derivatives. *Chem. Sci.* **2017**, *8*, 6433−6438; (c) Li, G.; Lei, P.; Szostak, M. Transition-Metal-Free Esterification of Amides via Selective N–C Cleavage under Mild Conditions. *Org. Lett.* **2018**, *20*, 5622−5625; (d) Liu, Y. M.; Shi, S. C.; Achtenhagen, M.; Liu, R. Z.; Szostak, M. Metal-Free Transamidation of Secondary Amides via Selective N–C Cleavage under Mild Conditions. *Org. Lett.* **2017**, *19*, 1614−1617.

(18) Song, L.; Cao, G-M.; Zhou, W-J.; Ye, J-H., Zhang, Z.; Tian, X-Y.; Lia, J.; Yu, D-G. Pd-catalyzed carbonylation of aryl C–H bonds in benzamides with CO_2. *Org. Chem. Front*. **2018**, *5*, 2086–2090.

(19) Kunieda, T.; Abe, Y.; Iitaka, Y.; Hirobe, M. Highly Stereo and Regioselective Formation of 2-Oxazolone Telomers, Potential Synthetic Intermediates for Amino Sugars. *J. Org. Chem*. **1982**, *47*, 4291-4297.

(20) Zou, Y.; Wang, Y.; Wang, F.; Luo, M.; Li, Y.; Liu, W.; Huang, Z.; Zhang, Y.; Guo, W.; Xu, Q.; Lai, Y. Discovery of potent IDO1 inhibitors derived from tryptophan using scaffold-hopping and structure-based design approaches. *Eur. J. Med. Chem*. **2017**, *138*, 199-211.

(21) Ragnarsson, U.;Grehn, L.; Monteiro, L. S.; Maia, H. L. S.Mild Two-Step Conversion of Primary Amides to Alcohols by Reduction of Acylimidodicarbonates with Sodium Borohydride. *Synlett* **2003**, *15*, 2386–2388.

(22) Evans, V.; Mahon M. F.; Webster, R. L. A mild, copper-catalyzed amide deprotection strategy: use of *tert*-butyl as a protecting group. *Tetrahedron* **2014**, *70*, 7593–7597.

(23) Hu, J.; Zhao, Y.; Liu, J.; Zhang Y.; Shi, Z. Nickel-Catalyzed Decarbonylative Borylation of Amides: Evidence for Acyl C-N Bond Activation. *Angew. Chem. Int. Ed*. **2016**, *55*, 8718–8722.

(24) Krasovskiy, A.; Knochel, P. A LiCl-Mediated Br/Mg Exchange Reaction for the Preparation of Functionalized Aryl- and Heteroarylmagnesium Compounds from Organic Bromides. *Angew. Chem. Int. Ed*. **2004**, *43*, 3333–3336.

(25) Kim, H.; Park, S.; Baek, Y.; Um, K.; Han, G. U.; Jeon, D-H.; Han, S. H.; Lee, P. H. Synthesis of Diaryl Ketones through Oxidative Cleavage of the C−C Double Bonds in *N*-Sulfonyl Enamide. *J. Org. Chem*. **2018**, *83*, 3486−3496.

(26) Meng, M.; Yang, L.; Cheng K.; Qi, C. Pd(II)-Catalyzed Denitrogenative and Desulfinative Addition of Arylsulfonyl Hydrazides with Nitriles. *J. Org. Chem*. **2018**, *83*, 3275−3284.

(27) Akhbar, A. R.; Chudasama, V.; Fitzmaurice, R. J.; Powell, L.; Caddick, S. Acyl hydrazides as acyl donors for the synthesis of diaryl and aryl alkyl ketones.*Chem. Commun*. **2014**, *50*, 743−746.

(28) Wakaki, T.; Togo, T.; Yoshidome, D.; Kuninobu Y.; Kana, M. Palladium-Catalyzed Synthesis of Diaryl Ketones from Aldehydes and (Hetero)Aryl Halides via C−H Bond Activation. *ACS Catal*. **2018**, *8*, 3123−3128.

(29) Li, M. Wang C.; Ge, H. Pd(II)-Catalyzed Decarboxylative Cross-Coupling of Potassium Aryltrifluoroborates with α-Oxocarboxylic Acids at Room Temperature. *Org. Lett*. **2011**, *13*, 2062-2064.

(30) Gooßen, L. J.; Mamone, P.; Oppel, C. Catalytic Decarboxylative Cross-Ketonisation of Aryl- and Alkylcarboxylic Acids using Magnetite Nanoparticles. *Adv. Synth. Catal*. **2011**, *353*, 57–63.

(31) Ruan, J.; Saidi, O.; Iggo J. A.; Xiao, J. Direct Acylation of Aryl Bromides with Aldehydes by Palladium Catalysis. *J. Am. Chem. Soc*. **2008**, *130*, 10510–10511.

(32) Vechorkin O.; Hu, X. Nickel-Catalyzed Cross-Coupling of Non-activated and Functionalized Alkyl Halides with Alkyl Grignard Reagents. *Angew. Chem. Int. Ed*. **2009**, *48*, 2937 –2940.

(33) Dohi, S.; Moriyama K.; Togo, H. Practical one-pot preparation of ketones from aryl and alkyl bromides with aldehydes and DIH *via* Grignard reagents. *Tetrahedron* **2012**, *68*, 6557−6564.

(34) Kim, S. W.; Um, T.; Shin, S. Metal-Free Iodine-Catalyzed Oxidation of Ynamides and Diaryl Acetylenes into 1,2-Diketo Compounds. *J. Org. Chem*. **2018**, *83*, 4703−4711.

(35) Koppolu, S. R.; Naveen N.; Balamurugan, R. Triflic Acid Promoted Direct α-Alkylation of Unactivated Ketones Using Benzylic Alcohols *via* in Situ Formed Acetals. *J. Org. Chem*. **2014**, *79*, 6069−6078.