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RESEARCH ARTICLE

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A high-efficient method for the amidation of carboxylic acids promoted by triphenylphosphine oxide and oxalyl chloride

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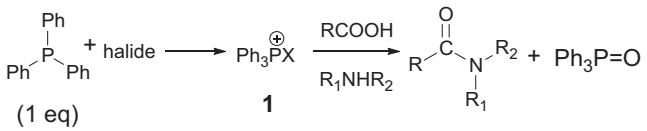
Abstract

A effective amidation reaction of carboxylic acids with various amines promoted by triphenylphosphine oxide and oxalyl chloride under mild and neutral conditions has been developed. The feature of this procedure was the using and recycling of triphenylphosphine oxide at room temperature in 0.5 h. Furthermore a plausible mechanism also be deduced with the help of ^{31}P NMR spectroscopy.

1 | INTRODUCTION

In nature, amides are fundamental building blocks in synthetic organic chemistry, natural products, pharmaceuticals, and agrochemicals; amides also have a wide range of applications in spices, dyes, plastics, textiles, and other industries. In this regard, the formation of amide bond has been extensively investigated. Amides are traditionally prepared from carboxylic acids and amines; generally, carboxylic acids should be preactivated by converting into reactive acid chlorides, anhydrides, active esters, or carboxylates before reacting with amines.[1–6]

Phosphonium, phosphinic salts, phosphonic acid derivatives and organophosphorus esters as efficient coupling reagents can promote the formation of amides.[7,8] Thus far, compounds such as PPh_3,[9–16] T3P,[17] $POCl_3$,[18] $P(OEt)_3$,[19] $P(OMe)_3$[20] have also been reported, in which the reaction mediated by PPh_3 and halogen has received increasing research attention. Up to now, halogen sources such as CCl_4,[9] CCl_3CN,[10] I_2,[11,20] NBS,[12] Br_2,[13] $BrCCl_3$[14] and CBr_4[15] have all been explored. These reactions confirmed that halophosphonium salts (Scheme 1, 1) as the intermediates could be rapidly generated from PPh_3 and halide, and this reagent was effective to amidation (Scheme 1). However, the concomitant generation of stoichiometric compound triphenylphosphine oxide (TPPO) by-products severely affects atom efficiency and large-scale applicability of these reactions. To overcome these drawbacks, Mecinovi′c[21] reported an organocatalytic amide bond formation reaction mediated by Ph_3P/CCl_4; in this reaction, TPPO is reduced into Ph_3P in situ (Scheme 2). Such in situ reduction of phosphorus oxides



SCHEME 1 PPh_3 with halide as coupling reagents for the amidation of carboxylic acids[9–16]

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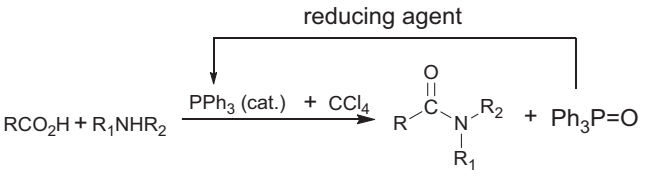
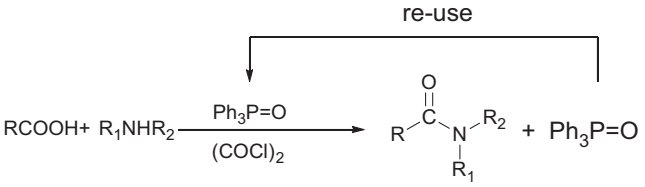


SCHEME 2 Ph_3P/CCl_4-promoted amidation of carboxylic acids followed by in situ reduction[21]



SCHEME 3 TPPO/$(COCl)_2$ applied to the amidation reaction by use and recycling of TPPO

has been exployed in several catalytic reaction, as the pioneer work of catalytic Wittig reaction by O'Brien and co-workers[22–25], and van Delft et al. developed the first catalytic Appel and Staudinger reaction[26,27]. This technique is effective, but its operating cost is high because of the harsh reagents and conditions required to regenerate phosphines and the complexity of the reaction system. Although most studies focused on the reduction of TPPO to TPP[28–30], we determining that the practical application of this waste product is more meaningful and important. Inspired by the conception of clean chemical reactions and promoted by the application of TPPO in previous studies[31–55], we hypothesize amidation reaction can be carried out at more easily and more conveniently condition with TPPO and $(COCl)_2$, that bypass the difficult TPPO reduction with a stoichiometric reductant and improve the atom efficiency of these reactions by recycle and re-use of TPPO (Scheme 3).

The chemistry of the TPPO/$(COCl)_2$ combination originally reported in 1977 by Fukui[33]. Then this reaction exploited by Denton and co-workers in Apple reaction and other reactions under Apple condition, and Gilheany also used it to the research of phosphine oxides reductions.[34–44]. however applied it into the amide reaction rarely mentioned[37,45,46], and high temperatures, complicated procedure and long reaction time are required. Hence, in the present study, we further exploited the application of TPPO and $(COCl)_2$ and used it to promote high-efficiently the amidation of carboxylic acids.

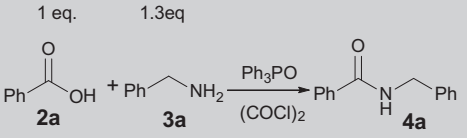
2 | RESULT AND DISCUSSION

Basing on previous reports[21], we explored reaction conditions with the model reaction between **2a** (1 equiv) and **3a** (1.3 equiv) and used TPPO (2 equiv)/$(COCl)_2$ (2 equiv) or TPPO (1 equiv)/$(COCl)_2$ (1.3 equiv) (Table 1, entry 1 and 2) as coupling reagent in toluene at 110°C. TLC analysis indicated that the reactants were consumed at 0.5 h; a 95% and 94.5% isolated yields of **4a** were obtained, respectively. The present study further optimized the reaction conditions through gradually reducing the reaction temperature. Finally, the desired product **4a** exhibited 94% yield even at room temperature (Table 1, entry 3). Many solvents (THF, $CHCl_3$, CH_2Cl_2, 1, 2-dichloroethane, and MeCN) (Table 1, entry 4-8 run1) are effective and the isolated yields of **4a** more than 85% in all cases. However, the yield will decrease to 85% if the ratio of carboxylic acid to amine is 1:1 at room temperature (Table 1, entry 9). Further modification involving decreasing the loading of TPPO to 50% and 75% had a detrimental effect on the yield (Table 1, entry 10 and 11). And at the end of these reactions, recovery rate of TPPO up to 91%. In addition, after the reaction (Table 1, entry 8 run1) completed, we added a certain amount of water-absorbing agent and reactants once again apart from TPPO to reactor. The yield of **4a** can be achieved to 89% after 0.5 h. Hence, a efficient and convenient method to synthesis of amides be exploited, in which TPPO can be reused and recycled (Table 1, entry 8 run2).

Montalbetti[3] reported that preparation of acyl chlorides can be rapid from their corresponding acids and $(COCl)_2$, moreover acyl chlorides are one of the easiest methods used to activate acid. Acyl chloride formation are often catalyzed by DMF, and an additional base is usually required when amines coupled with acyl chloride[56]. So a control reaction was established in the presence of 1.3 equiv. of $(COCl)_2$ and without TPPO; only 25% of **4a** were obtained from **2a** and **3a** even after 20 h at room temperature (Table 1, entry 12). Moreover, the 1 equiv. of TPPO and absence of $(COCl)_2$ were tested; only traces of **4a** were produced (Table 1, entry 13).

With this protocol, we explored the scope of the carboxylic acid substrates promoted by TPPO; the results are summarized in Table 2. Moderate to excellent yields were obtained for most cases. Firstly, a diverse set of para-substituted benzoic acids (Table 2, entry 1-5) reacted with **3a** to afford the corresponding amides that exhibit good to excellent isolated yields (more than 70%) but did not show an obvious electronic effect. With regard to the substitution pattern, higher yields were obtained when using chlorine (Table 2, entry 5) and nitro groups (Table 2, entry 3) in comparison with methyl (Table 2, entry 4) and methoxy (Table 2, entry 2). Furthermore, 1-naphthoic and phenylacetic acids also proceeded smoothly, affording the corresponding products with good yields (Table 2, entry 6-7). Only heterocyclic substituted carboxylic acid-picolinic acids showed comparatively low conversion (65%) efficiency for the reaction with benzylamine (Table 2, entry 8). Reactions in the absence of TPPO afforded lower isolated yields than that with TPPO.

TABLE 1 Optimization of triphenylphosphine Oxide promoted amidation reaction.[a]



Entry	$Ph_3PO/(COCl)_2$ (equiv)	Solvent	Temp (°C)	Yield[b] (%)
1	2/2	PhMe	110	95
2	1/1.3	PhMe	110	94.5
3	1/1.3	PhMe	25	94
4	1/1.3	THF	25	91
5	1/1.3	$CHCl_3$	25	90
6	1/1.3	CH_2Cl_2	25	88
7	1/1.3	$C_2H_4Cl_2$	25	89
8	1/1.3	MeCN	25	94 run1 89 run2
9[c]	1/1.3	MeCN	25	85
9	0.5/1.3	MeCN	25	50
10	0.75/1.3	MeCN	25	86
11[d]	0/1.3	MeCN	25	25
12[d]	1/0	MeCN	25	Trace

[a]Reaction was carried out with **2a** (5 mmol, 1 equiv), **3a** (1.3 equiv), solvent (5 mL) at the indicated temperature for 0.5 h.
[b]Isolated yield.
[c]**2a** (1 equiv) and **3a** (1 equiv).
[d]Time to over 20 h.

This result shows that TPPO facilitated the amide bond formation by generating halophosphonium salts with $(COCl)_2$.

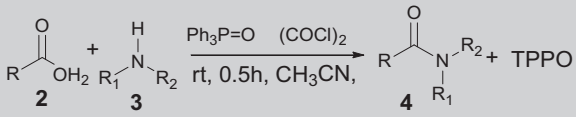
Both aliphatic amines (Table 2, entry 12, 13, 14, 17, 18) and aromatic amines (Table 2, entry 9, 10, 11, 15, 16) reacted with benzoic acid to generate products in good to excellent yields. Aliphatic amines (cyclohexylamine) can react with various benzoic acids to produce more than 70% isolated yields (Table 2, entry 12, 17, 18). In addition, aniline and 4-methoxy aniline that lower nucleophilic characteristics when compared with aliphatic amines reacted with **2a** under the optimal conditions in 94% and 72% conversion (Table 2, entry 9, 10). Moreover, the desired amide was obtained when benzoic acid reacted with secondary amines, including N-methyl aniline and diethylamine, with 75% and 68% isolated yields, which demonstrating that the conditions of the present study are also applicable to the synthesis of tertiary amides (Table 2, entry 11, 14). Whereas in the control experiments, only a small amount of amides was formed under the absence of TPPO even if after 20 h.

In order to elucidate the role of TPPO and $(COCl)_2$ and understand the reaction intermediates, ^{31}P NMR spectroscopy was used to detect the reaction process (Scheme 4). On the basis of that halophosphonium salts intermediate **1** could be generated by the reaction of TPPO and $(COCl)_2$[57] and intermediates acyl phosphonium **5** have been invoked previously[9,11,16,19,58,59], a plausible mechanism is deduced as shown in Scheme 4. Firstly, the solution of TPPO in MeCN showed a strong singlet at 29.26 ppm (Figure 1, I). Solid dissolved after addition of oxalyl chloride and a new signal appearance at 65.26 ppm (Figure 1, II), indicating the formation of chlorotriphenylphosphonium **1** (Godfrey et al.[60], δp=65.5 ppm). After adding benzoic acid **2a** for about 5 min, a new resonance was produced at δ=44.39 ppm (Figure 1, III). In the end, the addition of **3a** resulted in upfield shift of the resonance (δ=33.14 ppm) (Figure 1, IV). Through the post-processing, a sharp singlet at 29.26 ppm (Figure 1, I) appeared again.

3 | CONCLUSIONS

In summary, we successfully developed the triphenylphosphine oxide-promoted amidation under mild and neutral conditions, which can be also applied to industry. The reaction is easy to operate and effective for inactivated aromatic carboxylic acids and primary or secondary amines. And we believe that TPPO can be multiple used through added reactants one more time to reaction system. Significantly, TPPO was recyclable and only CO and CO_2 wasted in the end of reaction. And a plausible mechanism be derived by tracked the

TABLE 2 Scope of the amidation of **2** and **3**.[a]



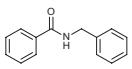
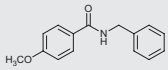
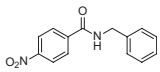
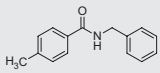
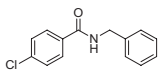
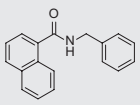
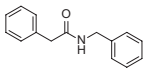
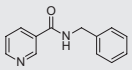
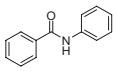
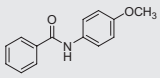
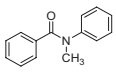
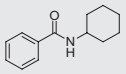
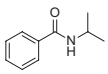
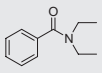
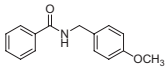
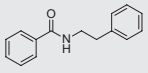
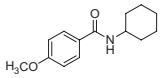
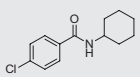
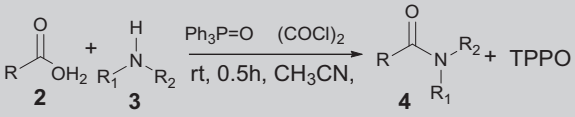
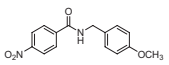
Entry	Amides	Products	Yield[b] (%)	Yield[c] (%)
1		**4a**	94	31[d] (25[e])
2		**4b**	91	41(36)
3		**4c**	81	10
4		**4d**	89	36
5		**4e**	90	3
6		**4f**	81	Trace
7		**4g**	74	Trace
8		**4h**	65	16
9		**4i**	94	2
10		**4j**	72	1
11		**4k**	75	Trace
12		**4l**	86	16
13		**4m**	80	3
14		**4n**	68	17
15		**4o**	97	35
16		**4p**	96	16
17		**4q**	70	17
18		**4r**	73	13

TABLE 2 (Continued)



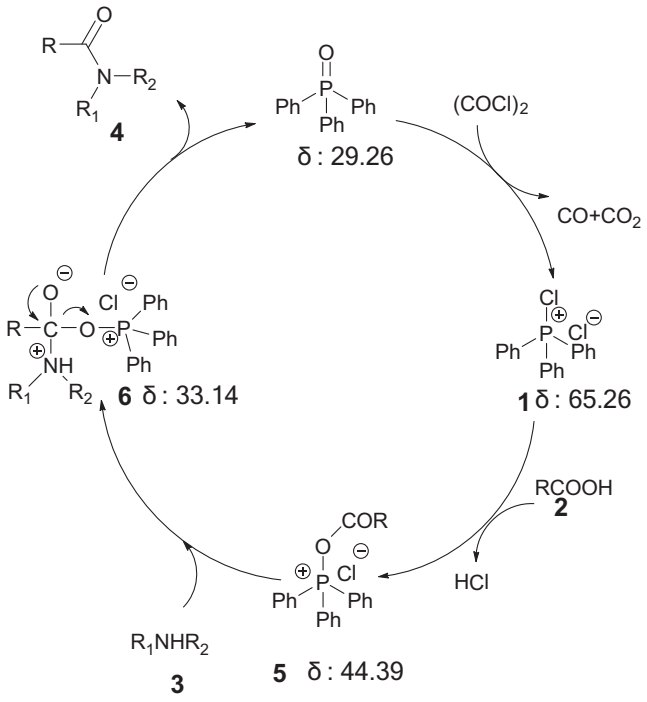
Entry	Amides	Products	Yield[b] (%)	Yield[c] (%)
19		**4s**	90	15

[a]Addition: To solution of Ph_3PO (1 equiv) in acetonitrile (3 mL) was added $(COCl)_2$ (1.3 equiv). After 10 min, **3** (1.3 equiv) in acetonitrile (2 mL) was added to solution after **2** (5 mmol, 1 equiv) added 5 min later, for 0.5 h at room temperature.
[b]Isolated yield.
[c]The reaction carried out without TPPO.
[d]Yield was determined by HPLC analysis.
[e]Isolated yield.

reaction with ^{31}P NMR spectroscopy. Due to these issues, the direct catalytic amidation of non-activated carboxylic acids with TPPO has attracted our attention. Further investigations to extend the application of TPPO are underway in our laboratory. Furthermore, in view of this method is simple and easy to operate, we anticipate our scheme can also be applied to more useful transformation, eg, the esterification reaction.

4 | EXPERIMENTAL

Chemicals were obtained from commercial sources and were used without further purification. The reaction was monitored by thin-layer chromatography carried out on silica gel plates (HSGF 254) and visualized under UV light (245 nm). Column chromatography was performed on 200-300 mesh silica gel. The ^1H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using chloroform-*d* ($CDCl_3$) (δ=7.28) as the solvent and TMS as an internal standard. ^{13}C NMR spectra were recorded on 125 MHz spectrometer using chloroform-*d* ($CDCl_3$) (δ=77.1 ppm) or dimethylsulfoxide-*d6* (DMSO-*d*) as the solvent with the central peak at 40.0 and TMS as an internal standard. Chemical shifts were reported in parts per million (ppm, δ) downfield from TMS. Data was manipulated directly via a networked PC with appropriate software. Splitting patterns are described as br=broad singlet, s=singlet, d=doublet, doublet of doublet (dd), t=triplet, q=quartet, m=multiplet. High-Resolution Mass Spectra (HRMS) were recorded on a Bruker (Fällanden, Switzerland) SolariX 70 FT ICR-MS spectrometer. HPLC analysis was performed on a Themo Scientific Dionex Ultimate 3000 (Waltham, MA, USA) HPLC system using C18, 5 μm, 120 Å (250×4.6 mm) column with acetonitrile: water as the mobile phase. Melting points were determined using Manon, MP120 Automatic melting point apparatus at a heating rate of 1°C /min.



SCHEME 4 Proposed mechanism of amidation mediated by TPPO and $(COCl)_2$

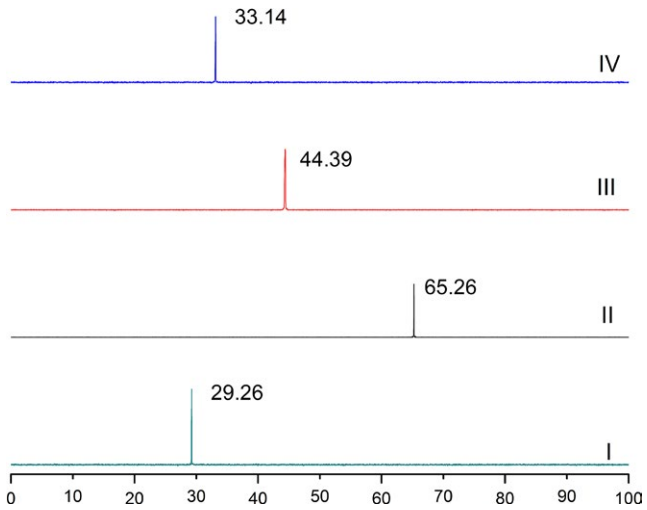


FIGURE 1 ^{31}P NMR spectra for synthesis **4a**. I: Ph_3PO (1 equiv), MeCN (3 mL). II: after addition of oxalyl chloride (1.3 equiv) to I. III: **2a** (5 mmol, 1 equiv) added to II. IV: **3a** (1.3 equiv) in MeCN (2 mL) was added to solution of III

4.1 | General procedure

Triphenylphosphine oxide (1.4 g, 5 mmol) and acetonitrile (2.0 mL) was added in 50 mL mouth flask, oxalyl chloride (0.55 mL, 6.5 mmol) was then added dropwise to the heterogeneous mixture. The resulting homogeneous, clear solution was stirred at room temperature for 10 min, at which time the appropriate acid (1 equiv, 5 mmol) added before the amine (1.3 equiv, 6.5 mmol) in acetonitrile (3 mL) added dropwise. The reaction was stirred at the same temperature for 0.5 h. The mixture was diluted with 100 mL of EtOAc, washed with three 50 mL saturated sodium hydrogen carbonate and the separated organic phase dried over anhydrous Na_2SO_4. Drying agent removed by filtrated and the solvent were evaporated in vacuo. Then the yield was then determined via purified by column chromatography using ethyl acetate / hexane (2:1) as eluent to give appropriate amide. All amide products presented in the article's Table 2 are previously known and reported compounds.

Procedure for (Table 1 entry 8 run2): Firstly, TPPO (1.4 g, 5 mmol), CH_3CN, $(COCl)_2$ (0.55 mL, 1.3 equiv, 6.5 mmol), benzoic acid (1 equiv, 5 mmol), benzylamine (1.3 equiv, 6.5 mmol) added to the reactor as the previous procedure. Reaction after half an hour at room temperature, 2 g anhydrous Na_2SO_4 was added. Then $(COCl)_2$ (0.55 mL, 1.3 equiv, 6.5 mmol), benzoic acid (1 equiv, 5 mmol), benzylamine (1.3 equiv, 6.5 mmol) added one more time. The reaction was stirred at the same temperature for 0.5 h. In the end, the yield was 1.88 g (89%).

4.1.1 | N-Benzylbenzamide (4a)

The product (0.96 g, 94% yield) was obtained as a white solid. mp 103.4-104.4°C [Wangngae et al.[61] 104-105°C]; ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 9.9 Hz, 4H), 7.33 (dd, J = 8.5, 4.2 Hz, 1H), 6.42 (s, 1H), 4.68 (d, J = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 138.2, 134.3, 131.5, 128.7, 128.5, 127.8, 127.5, 127.0, 44.0; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO$ 212.10699; found 212.10694.

4.1.2 | N-Benzyl-4-methoxybenzamide (4b)

The product (1.11 g, 91% yield) was obtained as a white solid; mp 127.3-128.7°C [Green et al.[62] 128-130°C]; ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.6 Hz, 2H), 7.43-7.30 (m, 5H), 6.94 (d, J = 8.6 Hz, 2H), 6.33 (s, 1H), 4.66 (d, J = 5.5 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 162.2, 138.5, 128.8, 128.7, 127.8, 127.4, 126.6, 113.7, 55.4, 44.0; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}NO_2$ 242.11756; found 242.11709.

4.1.3 | N-Benzyl-4-nitrobenzamide (4c)

The product (1.04 g, 81% yield) was obtained as a light yellow solid; mp 139.0-139.9°C [Bahrami et al.[63] 139-140°C]; ^1H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.38 (dd, J = 20.0, 6.1 Hz, 5H), 6.47 (bs, 1H), 4.70 (d, J = 5.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 149.5, 139.9, 137.5, 128.9, 128.2, 127.9, 123.7, 44.4; HRMS (FT ICR-MS) m/z: $[M-H]^+$ calcd for $C_{14}H_{12}N_2O_3$ 255.076419; found 255.07993.

4.1.4 | N-Benzyl-p-methylbenzamide (4d)

The product (1.01 g, 89% yield) was obtained as a white solid; mp 133.3-134.1°C [Kim et al.[64] 133-134°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 4.2 Hz, 4H), 7.33 (dd, J = 8.4, 4.1 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 6.37 (s, 1H), 4.67 (d, J = 5.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.4, 141.9, 138.4, 131.5, 129.2, 128.7, 127.8, 127.5, 127.0, 44.0, 21.4; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}NO$ 226.122641; found 226.12224.

4.1.5 | N-Benzyl-4-chlorobenzamide (4e)

The product (1.10 g, 90% yield) was obtained as a white solid; mp 162.7-163.4°C [Green et al.[62] 161-163°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.41-7.30 (m, 5H), 6.37 (s, 1H), 4.66 (d, J = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 137.9, 137.8, 132.7, 128.8, 128.4, 127.9, 127.7, 44.2; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}NOCl$ 246.068018; found 246.06766.

4.1.6 | N-Benzyl-1-naphthamide (4f)

The product (1.06 g, 81% yield) was obtained as a white solid; mp 124.3-124.8°C [Kim et al.[64] 120-122°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 8.3 Hz, 1H), 7.92 (dd, J = 24.2, 8.1 Hz, 2H), 7.59 (m, J = 22.2, 18.5, 7.2 Hz, 3H), 7.52-7.31 (m, 6H), 6.30 (s, 1H), 4.77 (d, J = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 138.1, 134.2, 133.7, 130.7, 130.1, 128.8, 128.3, 127.8, 127.6, 127.1, 126.4, 125.4, 124.9, 124.6, 44.0; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{18}H_{15}NO$ 262.12264; found 262.12232.

4.1.7 | N-Benzyl-2-phenylacetamide (4g)

The product (0.84 g, 75% yield) was obtained as a white solid; mp 120.9-121.4°C [Valeur and Bradley[65] 119-121°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (t, J = 7.3 Hz, 2H), 7.34-7.26 (m, 6H), 7.20 (d, J = 7.3 Hz, 2H), 5.78 (s, 1H), 4.43 (d, J = 5.7 Hz, 2H), 3.65 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 138.1, 134.8, 129.4, 129.0, 128.6, 127.5, 127.4, 127.4, 43.8, 43.6; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}NO$ 226.122641; found 226.12232.

4.1.8 | N-Benzyl-2-pyridinecarboxamide (4h)

The product (0.69 g, 65% yield) was obtained as a light yellow solid; mp 81.0-81.9°C [Lamar and Liebeskind[66] 81°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (d, J = 4.3 Hz, 1H), 8.44 (s, 1H), 8.25 (d, J = 7.8 Hz, 1H), 7.85 (td, J = 7.7, 1.6 Hz, 1H), 7.42 (ddd, J = 7.5, 4.8, 1.0 Hz, 1H), 7.40-7.32 (m, 4H), 7.29 (t, J = 7.0 Hz, 1H), 4.69 (d, J = 6.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 149.8, 148.1, 138.2, 137.3, 128.7, 127.8, 127.4, 122.3, 43.5; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}N_2O$ 213.102239; found 213.10176.

4.1.9 | N-Phenylbenzamide (4i)

The product (0.93 g, 94% yield) was obtained as a yellow solid; mp 161-162°C [Wangngae et al.[61] 162-163°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 7.4 Hz, 2H), 7.84 (s, 1H), 7.67 (d, J = 7.9 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, DMSO): δ 166.0, 139.6, 135.4, 132.0, 129.2, 129.0, 128.8, 128.1, 124.1, 120.8, 114.3, 40.5, 40.3, 40.1, 40.0, 39.8, 39.6, 39.5; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO$ 198.091340; found 198.09106.

4.1.10 | N-(4-methoxyphenyl)benzamide (4j)

The product (0.81 g, 72% yield) was obtained as a white solid; mp 154.1-155.0°C [Duangkamol et al.[67] 153-154°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 7.4 Hz, 2H), 7.75 (s, 1H), 7.56 (d, J = 7.3 Hz, 3H), 7.51 (t, J = 7.5 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 165.5, 156.0, 135.5, 132.7, 131.8, 128.8, 128.0, 122.4, 114.2, 55.6; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO$ 228.10191; found 228.10134.

4.1.11 | N-menthyl-N-phenylbenzamide (4k)

The product (0.79 g, 75% yield) was obtained as a light yellow oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J = 7.3 Hz, 2H), 7.15 (dd, J = 10.3, 5.0 Hz, 3H), 7.12-7.03 (m, 3H), 6.99 (d, J = 7.6 Hz, 2H), 3.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 144.8, 135.9, 129.5, 129.1, 128.6, 127.7, 126.8, 126.4, 38.3; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO$ 212.10699; found 212.10648.

4.1.12 | N-Cyclohexyl Benzamide (4l)

The product (0.87 g, 86% yield) was obtained as a white solid; mp 143.4-143.9°C [Wangngae et al.[61] 143-144°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 5.97 (s, 1H), 4.12-3.89 (m, 1H), 2.06 (d, J = 9.4 Hz, 2H), 1.78 (d, J = 13.4 Hz, 2H), 1.68 (d, J = 12.9 Hz, 1H), 1.46 (dd, J = 25.0, 12.4 Hz, 2H), 1.34-1.24 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.6, 135.1, 131.2, 128.4, 126.8, 48.7, 33.2, 25.5, 24.9; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}NO$ 204.138291; found 204.13761.

4.1.13 | N-Isopropylbenzamide (4m)

The product (0.64 g, 80% yield) was obtained as a white solid; mp 98.0-98.9°C [Liang et al.[68] 99-101°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 5.98 (s, 1H), 4.44-4.18 (m, 1H), 1.28 (d, J = 6.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 134.9, 131.2, 128.4, 126.9, 41.9, 22.7; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{10}H_{13}NO$ 164.106990; found 164.106151.

4.1.14 | N, N-Diethylbenzamide (4n)

The product (0.60 g, 68% yield) was obtained as colourless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (s, 5H), 3.50 (s, 2H), 3.21 (s, 2H), 1.21 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 137.1, 129.0, 128.3, 126.1, 43.2, 39.2, 14.1, 12.8; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO$ 178.122641; found 178.122048.

4.1.15 | N-(4-Methoxybenzyl)benzamide (4o)

The product (1.17 g, 97% yield) was obtained as a white solid; mp 94.9-95.9°C [Kim et al.[64] 95-97°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.58 (s, 1H), 4.58 (d, J = 5.6 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.3, 159.1, 134.4, 131.5, 130.3, 129.2, 128.5, 126.9, 114.1, 55.3, 43.6; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}NO_2$ 242.117555; found 242.11701.

4.1.16 | N-Phenethylbenzamide (4p)

The product (1.11 g, 98% yield) was obtained as a white solid; mp 116.7-117.4°C [Boehner et al.[69] 113-116°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.27 (t, J = 7.0 Hz, 3H), 6.25 (s, 1H), 3.74 (q, J = 6.7 Hz, 2H), 2.96 (t, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 138.9, 134.6, 131.4, 128.8, 128.7, 128.5, 126.8, 126.6, 41.1, 35.7; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}NO$ 226.12264; found 226.12199.

4.1.17 | N-Cyclohexyl-4-methoxybenzamide (4q)

The product (0.82 g, 71% yield) was obtained as a white solid; mp 160.3-160.8°C [Wangngae et al.[61] 159-160°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 7.3 Hz, 2H), 6.97-6.85 (m, 2H), 5.95 (s, 1H), 3.93 (d, J = 43.8 Hz, 1H), 3.85 (s, 3H), 2.02 (s, 2H), 1.76 (d, J = 12.8 Hz, 2H), 1.66 (d, J = 10.0 Hz, 1H), 1.43 (d, J = 10.0 Hz, 2H), 1.34-1.16 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 161.9, 128.6, 127.3, 113.6, 55.3, 48.6, 33.3, 25.6, 24.9; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{19}NO_2$ 234.148855; found 234.148994.

4.1.18 | 4-Chloro-N-cyclohexylbenzamide (4r)

The product (0.86 g, 73% yield) was obtained as a white solid; mp 187.7-188.5°C [Wangngae et al.[61] 186-187°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 5.94 (s, 1H), 4.07-3.89 (m, 1H), 2.05 (d, J = 9.8 Hz, 2H), 1.78 (d, J = 13.4 Hz, 2H), 1.67 (d, J = 24.1 Hz, 1H), 1.45 (dd, J = 25.0, 12.3 Hz, 2H), 1.25 (dd, J = 23.5, 10.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 137.4, 133.4, 128.7, 128.3, 48.8, 33.1, 25.5, 24.9; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}NOCl$ 238.099318; found 238.099117.

4.1.19 | N-(4-methoxybenzyl)-4-nitrobenzamide[1] (4s)

The product (1.28 g, 90% yield) was obtained as a light yellow solid; mp 136.5-137.0°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H), 7.34-7.27 (m, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.47 (s, 1H), 4.61 (d, J = 5.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 159.4, 149.6, 140.0, 129.4, 128.1, 123.8, 114.3, 55.3, 44.0; HRMS (FT ICR-MS) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NO$ 287.102633; found 287.101863.

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SUPPORTING INFORMATION

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